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# INTEGRATED OPTIC SENSOR FOR CROPLAND AMMONIA VOLATILIZATION MEASUREMENT

## ABSTRACT

Nitrogen (N) fertilizer accounts for 25 to 33% of the energy requirements in modern crop agriculture in the world today (Lemon and Van Houtte 1980). Energy input for the manufacture of these N fertilizers is in the range of 460 $\times 10^{12}$ Btu per year (Davis and Boudin 1977; Boswell *et al*. 1985). Unfortunately, for some N sources up to 70% of this energy in the form of $NH_3$ can be lost through improper application techniques and poor N management strategies.

Because it is a gas at atmospheric pressure, anhydrous $NH_3$ may be lost to the atmosphere during and after placement due to soil conditions and the depth and spacing of placement. Inadequate soil conditions, improper injector settings, and erroneous injection rates enhance this loss. Moreover, urea and urea-ammonium nitrate solution (UAN) are becoming the principal N sources for broadcast as well as placement application in agriculture. These sources are often not incorporated into the soil and may be less efficient sources of N fertilizers because of N loss via gaseous $NH_3$. Measurement of this volatile N is difficult, especially under field conditions. However, a precise and convenient method of measuring gaseous $NH_3$ near and above the soil surface is prerequisite to the development and evaluation of alternative fertilizer management strategies and application techniques which can reduce the potential for significant loss.

Recent advances in integrated-optic (IO) based sensing offers the potential of measuring low levels of $NH_3$ loss from a cropping system in the range of 100 ppb. The integrated design of an IO system allows for a more durable device that can be mass produced at low cost. Utilization of this sensor technology may be a feasible approach but must be tested under practical conditions to assess accuracy and reliability.

Under a grant from the Office of Industrial Technologies, U. S. Department of Energy, a project has been undertaken to develop an integrated-optic (IO) sensor for monitoring $NH_3$ evolution from agricultural land. The project is divided into three phases: Phase I: laboratory and bench-scale research for the development of the basic sensor, Phase II: the development and testing of a field prototype, and Phase III: field evaluation of the device in an agricultural setting.

## LITERATURE REVIEW

### Agricultural Nitrogen Applications

The application of N fertilizer to a cropping system accounts for up to one-third of the overall energy requirement of that system. Nitrogen application will vary with soil type, weather conditions, type of crop, and age of crop. The form in which the N is applied varies from broadcast granular fertilizers to sprayed low-pressure or non-pressure liquids to injected anhydrous $NH_3$ (high-pressure liquid).

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**Nitrogen Losses**

The process by which N is lost from the soil surface as $NH_3$ gas is termed $NH_3$ volatilization. Ammonia volatilization may occur when ammoniacal or ammonium-forming fertilizer is applied to the soil surface or when crop residues of high N content are returned to the soil surface without incorporation. These are common management practices with sod crops and in no-tillage crop production.

Losses under field conditions generally are in the range of 10 to 50% of the applied N, but they can be as great as 60 to 70%. Since N fertilizer application rates are usually in the range of 90 to 270 lb acre$^{-1}$ (100 to 300 kg ha$^{-1}$), $NH_3$ volatilization represents a substantial N loss from the soil-plant system. Nitrogen losses through $NH_3$ volatilization will vary with crop, soil conditions, and weather. Harper et al. (1983) reported $NH_3$ concentrations of up to 2.5 ppm (1800 $\mu$g m$^{-3}$) after urea application on a grazed sub-tropical cattle pasture system representing annual $NH_3$ losses of 24 percent of the applied urea N. Similarly, $NH_3$ losses of approximately 21% of the N fertilizer applied were detected from no-till wheat fertilized with ammonium nitrate (Harper et al. 1987). Hargrove et al. (1987) noted $NH_3$-N losses of up to 72% on a mulched soil surface treated with urea N.

Factors in the soil that influence the volatilization of $NH_3$ include soil pH, soil hydrogen ion ($H^+$) buffering capacity and cation-exchange capacity, and urease activity. When ammonium salts or ammonium-forming fertilizers are added to soil, ammonium ions ($NH_4^+$) and $NH_3$ are in equilibrium in the soil solution according to reaction (1). The

$$NH_4^+ \longleftrightarrow NH_3 + H^+ \qquad (1)$$

activity of $H^+$ ions, or the pH, largely determines the ratio of $NH_3$ to $NH_4^+$. At pH 9.3, the ratio is about 1:1. At pH values greater that 7.0, significant $NH_3$ volatilization can occur, but as long as pH remains less that 7.0, $NH_3$ losses are generally insignificant.

Soil pH is subject to rapid change following fertilizer applications, resulting from microbial activity and other chemical factors. A soil property more important than initial soil pH in determining $NH_3$ loss potential is the capacity of the soil to resist changes in pH, or its $H^+$ buffering capacity. The amount of buffering between the initial soil pH and a pH of about 7.5 is more directly related to the expected $NH_3$ loss than to the initial soil pH. Soil cation-exchange capacity is also important because it allows $NH_4+$ ions to be removed from soil solution, thereby reducing the total amount of $NH_3$ subject to volatilization. Soils with high pH but also a high cation-exchange capacity actually lose only a small amount of $NH_3$.

Urease is the enzyme which converts urea to $NH_3$ and $CO_2$. It is produced by both higher plants and microorganisms and occurs in soil both in living organisms and as free enzyme external to living organisms. Abundant urease and rapid urea hydrolysis results in an increased potential for $NH_3$ loss, since this generally results in increased pH and greatly increased concentrations of $NH_4^+$ ions. The following factors have been found to influence urease activity: (1) Soil organic matter content: as organic carbon increases, urease activity also increases. (2) Soil pH: the optimum soil pH for urease activity is between 7 and 9, with reduced activity at very acid (<5.0) and very alkaline (>9.0) pH values. (3) Soil temperature: generally, urease activity increases as temperature increases over the range of

50 to 149°F (10 to 65°C) and decreases above 149°F (65°C). (4) Soil water content: urease activity generally increases with increasing moisture content up to field capacity; at soil water potentials less than - 15 atm ($-5 \times 10^5$ pascal), urease activity is considerably reduced; a negative effect at moisture contents above field capacity has also been reported. (5) Urea concentration: an increase in urease hydrolysis rates usually accompanies high rates of urea application.

Although urease activity varies considerably from soil to soil and under various climatic regimes, urease concentration seldom limits $NH_3$ volatilization under field conditions. Generally, environmental factors are more important than urease concentration in determining total $NH_3$ losses under field conditions. Environmental influences on the loss of $NH_3$ include temperature, soil water content, and air exchange. Under controlled conditions, $NH_3$ losses increase with increasing temperature over the range of 41 to 113°F (5 to 45°C). This is due to temperature effects on chemical and biological reactions, especially on urease activity. However, the influence of temperature on $NH_3$ loss under field conditions is quite complex and is also closely related to soil water content.

The influence of soil water content has been most difficult for scientists to quantify in a consistent manner under dynamic field conditions, especially where the soil water content fluctuates widely on a diurnal basis because of the combined effects of dew formation and evaporation. However, from research conducted under field conditions, several relationships have emerged. (1) For maximum $NH_3$ loss rates, the soil water content must be at or near field capacity at the time of fertilizer application. If the soil is dry, dissolution of dry fertilizer materials is very slow, and thus the biological and chemical reactions necessary for $NH_3$ volatilization are very slow or do not occur at all. (2) On a diurnal basis, maximum $NH_3$ loss rates occur when the soil surface is drying. As the soil dries, the concentration of $NH_4^+$ and $NH_3$ in the soil solution increases, resulting in $NH_3$ being lost to the atmosphere to maintain equilibrium. (3) If the soil surface dries but is not rewetted by dew or light rainfall, $NH_3$ loss is reduced because of insufficient moisture for the necessary biological and chemical reactions. (4) If rainfall is sufficient to move the N source into the soil profile, $NH_3$ volatilization ceases. The exact amount of rainfall necessary to ensure no $NH_3$ loss depends on soil type, but for most soil types is 0.4 to 0.8 in (1 to 2 cm).

Considering all of these relationships, the influence of soil water content can be summarized as follows: On a diurnal basis, high $NH_3$ loss rates are generally associated with periods of rapid soil drying as long as the soil is not too dry initially, but high total $NH_3$ losses are associated with an initially moist surface soil followed by several days with no or small rainfall events.

Air exchange at the soil surface is also an important factor that influences the $NH_4^+/NH_3$ equilibrium and has been overlooked by many researchers. In laboratory systems, it was found that relative $NH_3$ losses were maximum when the air exchange rate was at least 10 chamber volumes per minute (the air above the soil was completely replaced ten times per minute). Field measurement techniques that utilize enclosures generally do not allow normal air exchange and thus do not mimic field conditions effectively.

### Current Techniques for Monitoring

The four techniques for field measurement of $NH_3$ volatilization are forced-draft techniques (Hargrove et al. 1987); micrometeorological techniques (Denmead et al. 1977 and Harper et al. 1987); recovery of $^{15}N$, a stable, naturally occurring N isotope (Hargrove et al. 1987); and plant response. The forced-draft and micrometeorological techniques involve direct measurement of volatilized $NH_3$, while the $^{15}N$ recovery and plant response methods are indirect methods.

The two direct methods utilize wet chemistry analyses to provide $NH_3$ concentrations. These techniques are tedious and time consuming and cannot provide "real-time" monitoring of $NH_3$ losses from a crop. Furthermore, the techniques also do not avail themselves as a practical, farm-use tool for the management of N. Therefore, the development of improved N management and application strategies is hindered by the lack of responsive monitoring techniques.

### Electronic Sensor Technologies

Technologies that are commercially available for continuously monitoring atmospheric $NH_3$ levels include metal oxide semiconductor (MOS), electrochemical, and photoionization. MOS based sensors work on the principal of ionoadsorbtion whereby oxidation reduction type reactors at the sensor surface has the result of altering the gross conductive properties of the material (Clifford and Tuma 1982). The effect can be measured as a change in resistance. While they have been used for monitoring $NH_3$ levels below 100 ppm (70 mg $m^{-3}$), MOS sensors are temperature sensitive and are not very species specific. These sensors can be mass produced at a cost of approximately $500; however, performance at levels below 10 ppm (7 mg $m^{-3}$) is very suspect.

Electrochemical $NH_3$ sensors, while more species specific through the use of special electrolytes and gas-permeable membranes, are subject to interference from temperature and humidity changes (Ross and Daley 1986; Ross 1987). Moreover, sensor response and sensitivity is not sufficient to monitor $NH_3$ levels below 1 ppm (0.7 mg $m^{-3}$). These sensors, in their current form, are not in the form for mass production and currently cost in the range of $1,200 to $2,500.

Photoionization based sensors involve the process of exposing trace molecules to an ultraviolet light source which are in turn collected and measured for a proportional concentration reading. Interference from atmospheric UV could be a problem. These sensors typically cost over $10,000.

### Integrated-Optic Chemical Sensors

Optical sensors have recently been demonstrated as capable of measuring soil organic matter levels rapidly and accurately. In this case, the sensor transponder was mounted to a tractor tool bar and inserted into the soil as the tractor moved through a field (Gaultney et al. 1988).

Integrated-optics (IO) is a relatively new optical waveguide technology developed in the early 1970s with much of the early emphasis devoted to communication aspects and signal processing applications (Verber 1984 and Alferness 1984). It relies on planar waveguide structures rather than the more familiar cylindrical optical fiber configuration. The planar waveguide consists of a thin layer of slightly higher refractive index material formed or deposited on the surface of a planar substrate. Direct access to the waveguide surface provides distinct advantages as thin film elements may be incorporated into or on the waveguide surface to create two dimensional optical systems capable of performing all the functions of standard bulk optical systems. More importantly, access to the waveguide surface provides the basis for innovative sensor configurations relying on the interaction of a guided optical beam with a cover or surrounding medium.

The basis of all the IO waveguide sensing techniques centers around the interaction of a guided light beam with the cover medium. The guided beam is characterized by a sinusoidal electric field distribution within the waveguide and an exponentially decaying tail (evanescent field) extending into the cover medium. Because the evanescent field of a guided wave penetrates the cover medium, it is sensitive to the optical properties of that medium. The IO chemical sensors may function with both liquids and gaseous mediums. Gaseous mediums are generally sensed by incorporating thin films on the surface of the waveguide that are interactive with the particular chemical species of interest, $NH_3$ for example (Giuliani et al. 1983). The interaction of the guided beam with the chemically selective film on the waveguide surface may manifest itself through luminescence in the cover medium that is induced by the guided wave, by the attenuation of a guided beam (spectrally dependent absorption or scattering) and through changes in the phase properties of the guided beam. The latter mechanism provides the basis for an extremely sensitive detection scheme based on the use of IO interferometric configurations (Hartman 1990) or grating devices incorporated onto the surface of the waveguide (Tiefenthaler and Lukosz 1984).

A particularly useful IO chemical sensor configuration is based on a multi-moded waveguide configuration (Hartman 1990) and is the subject of an internally funded research program at the Georgia Tech Research Institute. A functional view of the cross-section of a multimode IO device is illustrated in Figure 1. Its operation depends on the existence of a few discrete guided modes which can exist in the case of a thin waveguide (thickness less than a few micrometers), all of which are excited by a common optical source. The differential nature of the device occurs because the evanescent field of the lowest order mode is confined to the waveguide (does not extend into the cover medium) while the evanescent field of the higher order mode extends into the cover medium. Thus, a comparison of the two modes, either interferometrically or by comparing intensities, provides a highly sensitive means of monitoring changes occurring in chemically selective cover film for example.

Experimental and analytical results have shown the IO multimode device is capable of highly sensitive differential absorption and differential interferometric measurements. The interferometric operation is achieved by interfering the lowest order mode with a higher order mode. A change in the refractive index of the cover film introduces a phase change into the higher order mode which causes a corresponding change in the output intensity of the interferometer. A change in the refractive index of the cover film of $10^{-5}$ will introduce a phase change of approximately 0.19 pi radians in the highest order mode of a four mode waveguide. That phase shift will, in turn, produce 10% change in the output intensity of 0.8 in (2 cm) pathlength interferometer (Hartman et al. 1988). Unlike other interferometric configurations, the IO devices can also be designed to minimize temperature dependence or sensitivity to mechanical disturbances and this accounts for the extremely high detection sensitivity available through the IO interferometric configurations.

### Chemically Selective Films For IO Sensing

In prior work on $NH_3$ sensors, the change in absorption has been used to detect the presence of $NH_3$ vapors. The change in absorption due to the color change in ninhydrin film coated onto a fiber optic waveguide was used to detect $NH_3$ concentrations below 100 parts per billion (ppb) (Orofino et al. 1977). However, this device was irreversible due to the chemistry involved. Also investigated was the absorption approach using an oxazine dye that changed from blue to red in the presence of $NH_3$. This device was sensitive to concentrations of 60 parts per million (ppm) with its sensitivity limited due to the interference of water vapor (Giuliani et al. 1983). To achieve detection sensitivities in the ppb range would require a significant reduction in the water vapor concentration. The system was quick to respond and reversible due to the weakly proton donating ability of the dye and the weakly basic $NH_3$.

In addition to absorption based detection, the multimode waveguide interferometric configuration offers an approach based on a change of the refractive index of the chemically selective film. This approach is attractive due to the high detection sensitivity of the IO interferometric configuration, indicating only very small amounts of $NH_3$ need to be absorbed. These coatings will be required to have some affinity for the $NH_3$ but this affinity should be weak enough so as to be reversible. Good candidates come from immonium salts, active methylenes, phenols, and any other compounds which have proton donating ability (pka) comparable to ammonium ($NH_4^+$). The reaction of these weakly acidic compounds with $NH_3$ bring about a change in the molecular structure which involves a change in index of refraction. The possible reagents would need to be investigated for the balance between their affinity and adduct stability in order to produce a quick response and reversibility.

The coating might be a thin reagent film; it could have the reagent incorporated in a polymer matrix, or it could be covalently bonded by functionalizing the waveguide surface. The best method will be dictated by the required index of the coating. In addition, the index of the waveguide can be tailored to meet any coating requirements.

In this study, organic chemicals were chosen for waveguide coatings based on their expected reactivity with gaseous $NH_3$ vapors and compatibility of their refractive index with the refractive index of the waveguide substrate materials currently being utilized. To achieve maximum detection sensitivity, the coating refractive index should be the same as or just slightly greater than the waveguide substrate index.

The most commonly used waveguide substrate material is BK-7 glass which has a refractive index of 1.515. To expand the list of potential coating materials, optical waveguides based on a glass with a lower refractive index are under development. The substrate material, obtained from Schott, has a refractive index of 1.46. The lower index will also facilitate optimization of detection sensitivity.

## PROJECT GOALS AND OBJECTIVES

The goal of this project is to develop a field-worthy sensor system to monitor gaseous $NH_3$-N transfer from agricultural cropland. Monitoring these losses would promote several avenues of $NH_3$ conservation including minimizing application losses due to poor equipment settings and improving application strategies through a better understanding of the relationship between fertilizer application and $NH_3$ volatilization. In both cases, an improvement in application efficiency and N utilization efficiency would reduce the amount of fertilizer applied resulting in significant cost and energy savings. Also, these goals could contribute to improved N managment as related to environmental pollution concerns.

The objectives of this study are divided into two separate phases:

**Phase I: Laboratory and Bench-Scale Research**

- Design and test an integrated-optic sensor for monitoring low levels of $NH_3$ under simulated field conditions.
- Determine the relationship between sensor output and simulator N losses.
- Develop alternative sensor uses, i.e. $N_2O$ or other gaseous N forms, dependent on adaptability for $NH_3$ monitoring.

**Phase II: Prototype Development**

- Develop the IO sensor system to a level suitable for field testing.
- Improve bonding between chemically sensitive cover medium and waveguide.
- Incorporate optical components into single integrated device.

**Phase III: Field Research**

- Conduct field tests of the sensor system to determine the accuracy and reliability of sensor system under field conditions.
- Use the sensor system to evaluate alternative management strategies for improving fertilizer N use efficiency.
- Evaluate the sensor for potential use by commercial anhydrous $NH_3$ applicators to monitor $NH_3$ losses during application.

## RESULTS TO-DATE

### Absorption Device

In this study, both absorption and interferometric devices are being developed for detecting $NH_3$ in air. An absorption device is dependent on the attenuation of the guided light beam by spectrally dependent absorption or scattering. Absorption devices utilizing an oxazine dye (oxazine 720 perchlorate) as the cover medium are being evaluated.

Previous work by others indicated that oxazine dye was a potential indicator; however, it was limited by lengthy response times and humidity interference.

In this study, varying concentrations of oxazine 720 perchlorate are being spun onto a waveguide surface at thicknesses in the range of 500 angstroms. When $NH_3$ is present, the dye's absorption at the He Ne laser wavelength (633 nanometer) decreases. The graph in Figure 2 illustrates a peak in the output intensity from a photodetector during an exposure to $NH_3$ (500 ppm).

### Interferometric Device

Interferometric IO devices rely on the change of phase properties of the guided light beam as it interacts with the cover medium. The differential nature of the device occurs because the evanescent field of the lowest order mode is confined to the waveguide (does not extend into the cover medium) while the evanescent field of the higher order mode extends into the cover medium. A comparison of the two modes interferometrically provides a highly sensitive means of monitoring changes in the chemically selective cover medium. Figure 3 provides an illustration of a conceptual multimode IO sensor with a description of the guided wave evanescent field distribution.

Aniline salts are currently being evaluated as cover media candidates for an interferometric device. Like the oxazine dye, varying concentrations and formulations of an aniline salt solution are being spun onto a waveguide surface in submicron thicknesses. When the waveguide is exposed to $NH_3$, a change in the refractive index in the aniline salt occurs, resulting in a phase change in the guided beam derived from the He Ne laser. An example of this phase change is illustrated in the output graph in Figure 4.

### Design Considerations

The selection and deposition of these substrates onto a waveguide provide some of the major challenges in the development of the sensor. The concentration of the substrate in solution directly affects the degree of light scattering that takes place, thereby shadowing any response. Furthermore, the substrate must be deposited in very thin molecular layers by Langmuir Blodgett or similar deposition techniques in order to maintain the durability and stability of the substrate over long periods of time.

The mechanics of coupling of all of the sensor components (waveguide, diode laser, beam splitters, photodiodes), as illustrated in the example of an interferometric device in Figure 3, is also a major design consideration. Similarly, an absorption device would likely require a multipath design to increase the pathlength and, hence, the sensitivity of the device. Considerable design will also have to go into the evolution of a laboratory device into a field-hardened sensor capable of withstanding severe weather conditions, exposure to dust and chemicals, and mechanical stresses.

## FUTURE WORK

Phase I of the project is currently underway with the design and testing of a laboratory class sensor. The sensor development program will consist of three phases. Phase A will be initial screening tests where $NH_3$ in air is blown over the surface of the sensor to determine if a specific surface coating is a possible candidate for further testing. Phase B will be the testing of the sensor under varying environmental conditions in the sensor test chamber with $NH_3$ - air mixtures supplied from a double dilution dynamic gas mixing system. Phase C will be the testing of the sensor in the sensor test chamber with $NH_3$ - air mixtures resulting from the evolution of $NH_3$ from fertilizer amended soil in the soil test simulator. The sensor and candidate coatings will be evaluated for response, reversibility, and temperature, velocity, and humidity effects.

Phase B testing will determine the absolute detection levels of the candidate coatings selected during Phase A testing. The sensor will be mounted inside the sensor test chamber, and the chamber sealed. This same chamber and mounting technique will be used for the Phase C testing. A predetermined $NH_3$ - air mixture will be generated in the gas mixing system and introduced into the sensor test chamber.

Phase C will compare the output from the sensor with conventional wet chemistry analyses. The sensor will again be mounted on the top of the sensor test chamber. The $NH_3$ in air mixture will be generated inside soil test chambers. The gas exiting the sensor test chamber will be routed through an acid trap where the $NH_3$ will be collected for wet chemistry analysis.

If the basic device is demonstrated to be capable of measuring $NH_3$ at low ppm and ppb levels, the research will progress to Phase II. In Phase II, the physical characteristics of the sensor will be developed such as the bonding of the cover medium to the waveguide and the integration of optical components into a single device. If low ppb levels are not attainable with this device, more sophisticated techniques will be evaluated to enhance the sensitivity of the device including phase modulation or modification of the chemical substrate.

Once the prototype device is developed under Phase II, it will be subjected to two series of field trials at the University of Georgia-Griffin Station. The focus of these trials would be to establish the capability of the sensor in detecting the loss of $NH_3$ from soils after the application of anhydrous $NH_3$. It is anticipated that there will be commercial participation in both Phases II and III.

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## DISCLAIMER

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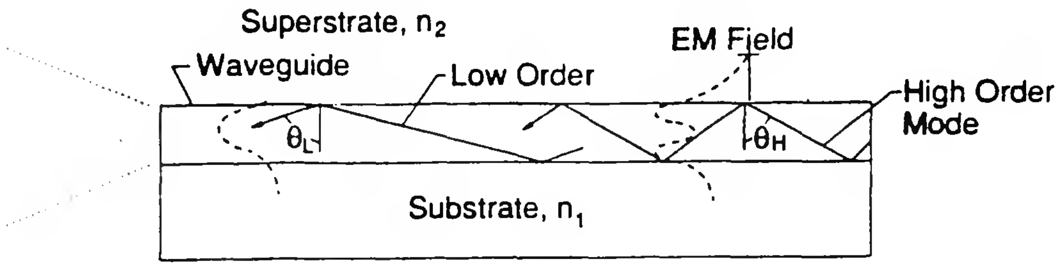

$\theta_L < \theta_H$

1) Waveguide modes characterized by an effective mode index

2) Higher order mode index - dependent on superstrate index

Figure 1. Functional View of a Multimode IO Waveguide Interferometer

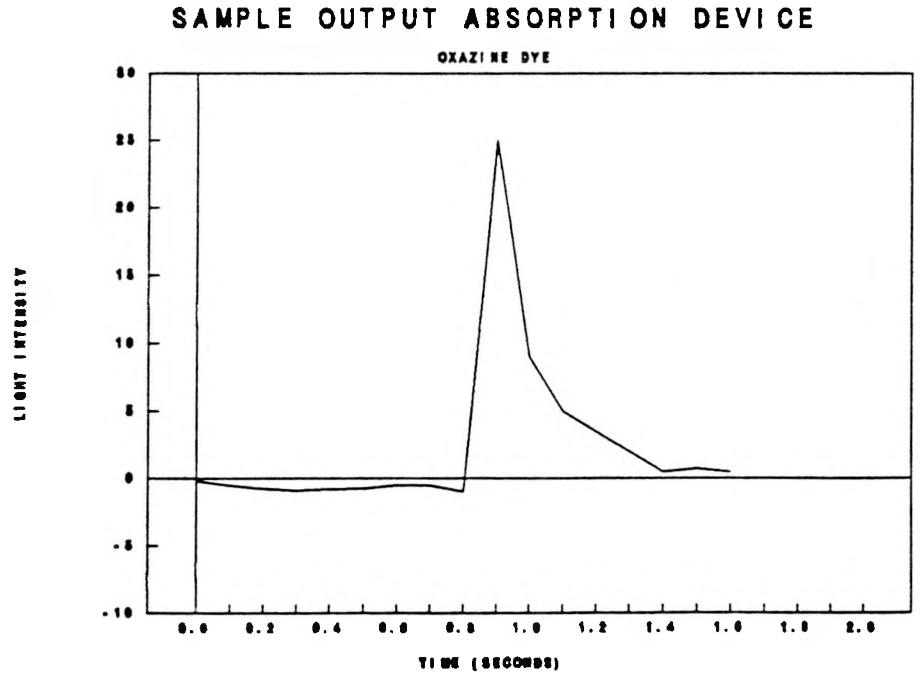

Figure 2. Example of Output from Absorption Device

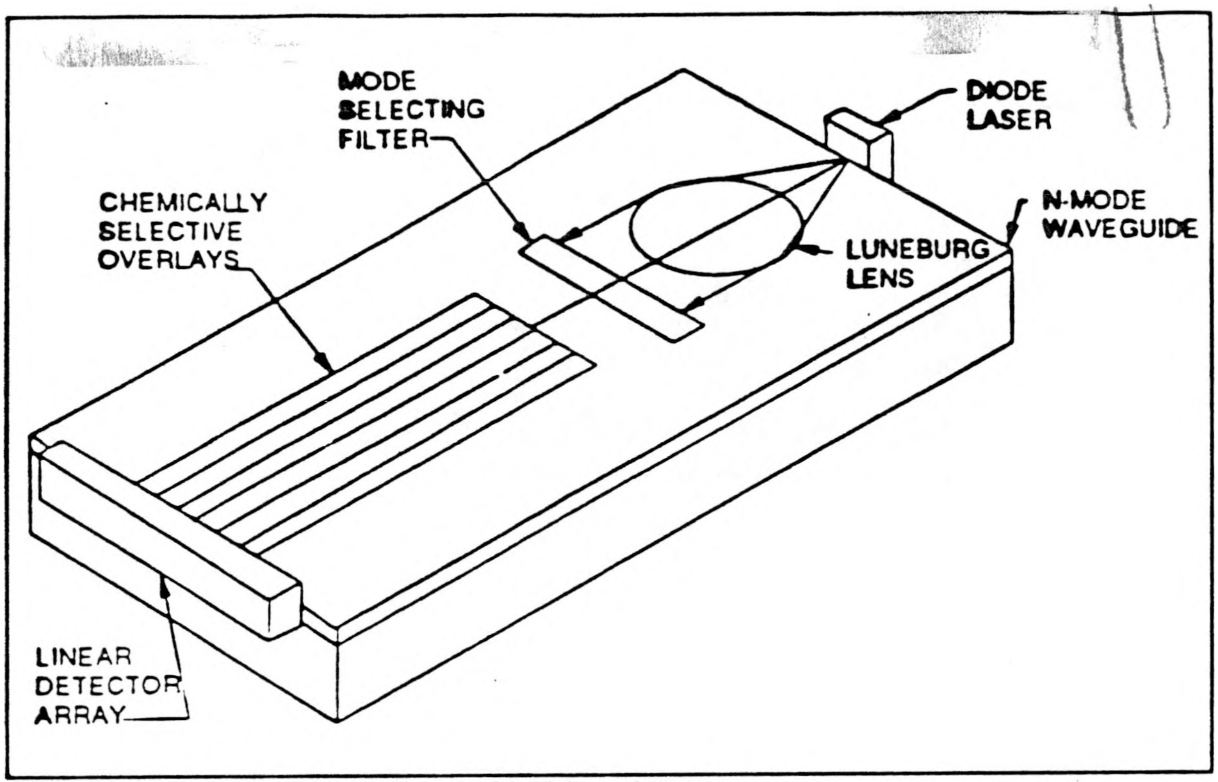

Figure 3. Conceptual Configuration of a Multichannel IO Sensor

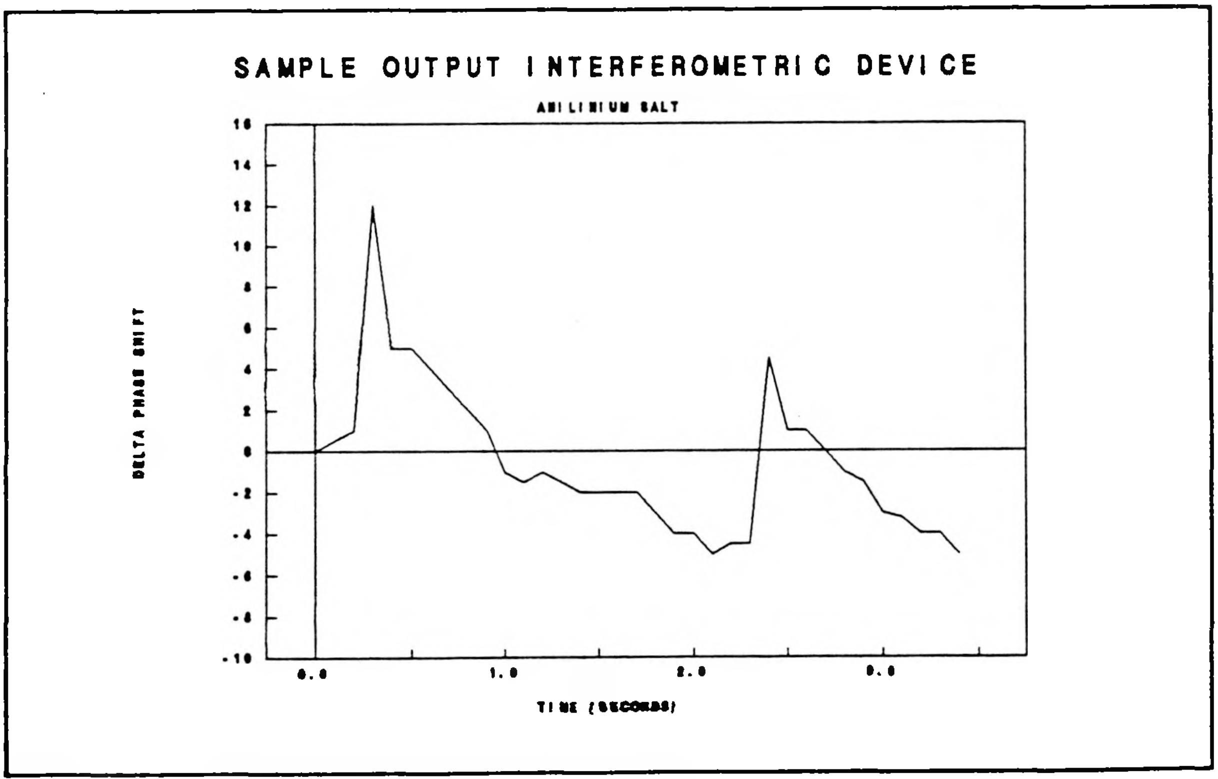

Figure 4. Example of Output from Interferometric Device