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Ammonia and Ammonium Hydroxide Sensors for Ammonia/Water Absorption Machines: Literature Review and Data Compilation

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Summary

The measurement of absorbent concentration is of great interest to researchers developing advanced absorption cycle systems. Absorbent concentration measurement is a key parameter in determining the performance of these absorption cycle machines. In binary refrigerant systems such as the ammonia/water cycle, *in situ* or remote sensing capabilities are needed to measure real-time concentrations of ammonia in water (NH_4OH).

This report describes an evaluation of various sensing techniques for determining the ammonia concentration in the working fluid of ammonia/water absorption cycle systems. Pacific Northwest Laboratory (PNL) researchers conducted the evaluation in collaboration with Battelle Columbus Operations as part of a project supported by the U.S. Department of Energy. The purpose of this work was to determine if any existing sensor technology or instrumentation could provide an accurate, reliable, and cost-effective continuous measure of ammonia concentration in water. The resulting information will be used for design optimization and cycle control in an ammonia-absorption heat pump.

PNL researchers evaluated each sensing technology against a set of general requirements characterizing the potential operating conditions within the absorption cycle. The criteria included the physical constraints for *in situ* operation, sensor characteristics, and sensor application. PNL performed an extensive literature search, which uncovered several promising sensing technologies that might be applicable to this problem. Sixty-two references were investigated, and 33 commercial vendors were identified as having ammonia sensors. The technologies for ammonia sensing are acoustic wave, refractive index, electrode, thermal, ion-selective field-effect transistor (ISFET), electrical conductivity, pH/colormetric, and optical absorption.

Based on information acquired in the literature search, PNL recommends that follow-on activities focus on ISFET devices and a fiber optic evanescent sensor with a colormetric indicator. The ISFET and fiber optic evanescent sensor are inherently microminiature and capable of *in situ* measurements. Further, both techniques have been demonstrated selective to the ammonium ion (NH_4^+). The primary issue remaining is how to make the sensors sufficiently corrosion-resistant to be useful in practice.

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Contents

1.0 Introduction

Absorption cycle chillers and heat pumps are commonly used only in applications where economies of scale work to the advantage of that design. These are applications requiring typically tens to hundreds of refrigeration tons (RT),(a) and the cycle most commonly used is based on lithium bromide/water absorption. In residential and small business applications, where the refrigeration requirements are typically on the order of 3 to 5 RT, devices using a vapor-compression cycle or air-to-air heat pumps are usually preferred. However, there are specialized applications in this capacity range where an ammonia-absorption heat pump offers unique advantages that can offset the disadvantages of larger size and generally higher cost.

In addition, the economics of the heating, ventilating, and air-conditioning (HVAC) industry are changing, partly in response to the changing regulatory climate regarding commercial use of fluids based on chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs). Consequently, ammonia-absorption cycles are beginning to look more attractive for small-scale heating and cooling applications, if the identified system performance problems can be overcome with new and improved designs.

To explore this potential, Battelle Columbus Operations (BCO) is developing an ammonia-absorption heat pump for residential and light commercial applications. The effort is supported jointly by the U.S. Department of Energy (DOE) and the Gas Research Institute (GRI).

The heat pump design is bounded by severe constraints in terms of the physical size of the unit, operational range, efficiency, material compatibility, and cost. Basically, it must be very small, capable of year-round operation without backup, reliable, environmentally benign, and no more expensive than currently available vapor compression refrigeration units.

To determine the performance of such a heat pump, it is imperative to obtain accurate measurement of absorbent concentration. In binary refrigerant systems such as the ammonia/water cycle, *in situ* or remote sensing capabilities are needed to measure real-time concentrations of ammonia in water (NH_4OH).

In support of the BCO effort, researchers at the Pacific Northwest Laboratory (PNL)(b) conducted a multifaceted study. The tasks involved reviewing current literature on ammonia concentration

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(a) The common unit of refrigeration capacity is the ton, based on the rate of heat transfer needed to freeze one ton of water at 32°F in 24 hours. In American engineering units, one ton of refrigeration is equivalent to 200 Btu/min, which is equivalent to 209.3 kJ/min in Systeme Internationale (SI) units. In metric units, one ton of refrigeration is equivalent to 50 kcal/min, which is equivalent to 210.96 kJ/min. Thus, for most engineering calculations, refrigeration in tons can be considered to be the same in SI and American engineering units.

(b) PNL is a multiprogram laboratory operated for the U.S. Department of Energy under Contract DE-AC06-76RLO 1830 by Battelle Memorial Institute.

sensors, developing the functional criteria for the sensor in the ammonia-water cycle heat pump application, and selecting an ammonia concentration sensor best suited to the heat pump application.

The primary objective of PNL's work was to identify a means of measuring ammonia concentration in the testing and design phase of heat pump development. A secondary objective was to identify a potential sensor or monitoring technology that could provide feedback control information in an operating commercial ammonia-absorption heat pump.

This report documents the project tasks performed by PNL. Section 2 presents a detailed description of the overall challenge being addressed by BCO and PNL. The literature review is documented in Section 3. PNL's approach to the search is summarized, and the relevant findings from the literature related to ammonia concentration sensor technology are briefly discussed. The functional criteria against which each sensor technology was evaluated are discussed in Section 4. The conclusions and recommendation based on the sensor review are presented in Section 5. Sections 6 and 7, respectively, contain lists of references cited and bibliographic materials consulted during this study. Supplementary materials are provided in Appendixes A through C.

2.0 Statement of Problem

A typical simple ammonia-absorption refrigeration cycle is illustrated in Figure 1. Battelle Columbus Operations has designed a prototype heat pump using this cycle, and test loops have been built for key components of the system. One test loop is designed to investigate the vapor generation components; another is to test the three main components of the regenerative/generative absorber part of the cycle.

The first loop includes the condenser as a test element, as well as the liquid pump for the concentrated NH_3-H_2O. The absorber portion of the test loop consists of a full-scale model of the generator/absorber exchanger (GAX), absorber heat exchanger (AHE), and hydronically cooled absorber (HCA) segments of the absorber. The system is appropriately instrumented to obtain temperatures, pressures, and flow rates of interest.

However, measurements of ammonia concentration are made only by manually sampling the fluid at the inlet and outlet and at one intermediate point. (Concentration is determined by chemical titration. The measurement represents a discrete sample from a specific location in the system at a specific sampling period.)

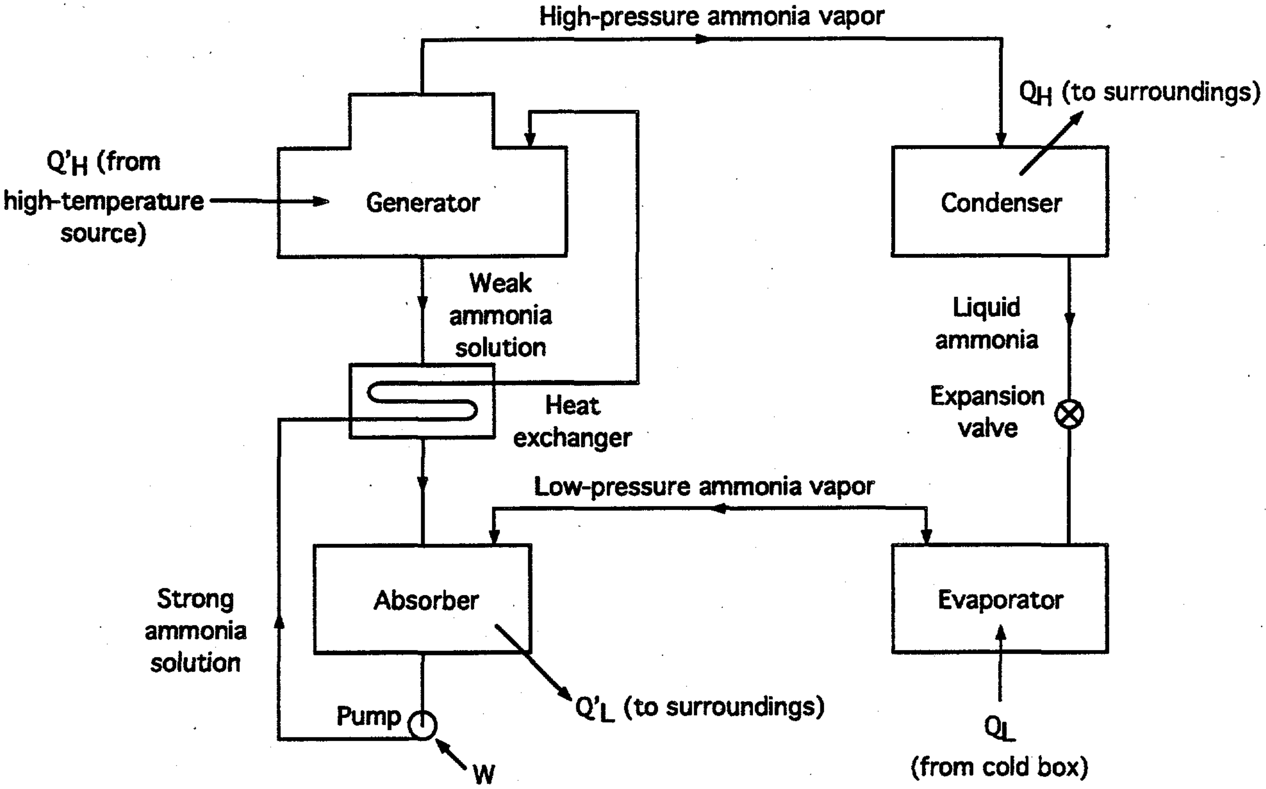

Figure 1. Ammonia Absorption Cycle

There is a critical need for an ammonia concentration sensor that would allow monitoring the rate at which ammonia is absorbed by the solution as it falls in a thin film over the coils of the absorber. The length of the coil is the most significant variable affecting the overall size of the system. The absorber must be long enough to obtain the desired ammonia concentration in the working fluid, but making it any longer than necessary represents excessive size and concomitant costs. The relationship between the flow rate of the ammonia vapor (which flows counter-current to the falling film), the flow rate of the absorbing solution, and the rate of absorption must also be measured to optimize the absorber design.

Ideally, a continuous reading of changing ammonia concentration is needed along the full length of the coils. It would also be useful to have information on the distribution of the ammonia concentration tangentially around the coil. If this distribution is not uniform for some reason, it could significantly affect the heat pump's performance. (The uniformity of the film itself also could be a factor in this.)

The ammonia concentration sensor needed is a device that could be mounted at a number of points on the absorber coil without interfering with the flow of the fluid film. For design purposes, the relative concentration of ammonia would be sufficient information. An absolute measurement of concentration is not essential, but repeatability is critical.

Without a sensor to give information on the dynamics of ammonia absorption and the spatial variation of ammonia concentration within the device, the BCO test loop can give only endpoint data on the test absorber. A reliable, repeatable, real-time measurement of the ammonia concentration as it changes during the absorption process is needed to provide data on the internal absorption process in the absorber. In addition to providing critical design information, such data would improve the usefulness of every absorber test conducted and could reduce the testing requirements.

2.1 Absorber Description

In the ammonia-absorption cycle, the absorber performs two important functions. In the first, the working fluid absorbs a higher concentration of ammonia. After leaving the absorber, this ammonia-water solution is pumped up to the high pressure in the system, where it is heated to separate it into its binary components, ammonia vapor (NH_3) and a low-concentration solution. (The main advantage of an absorption cycle over a vapor compression cycle is the savings in pumping power. Because the ammonia is dissolved in an aqueous solution, the fluid being pumped is in a liquid state, which generally requires less work than vapor compression.) In the second function, heat is generated in an exothermic reaction by the process of ammonia vapor being absorbed by the solution. This is technically waste heat (in the air-conditioning mode) but can easily be utilized in a regenerative cycle to provide some of the heat input required by the generator.

Two absorber arrangements are of interest. Each involves different combinations of the liquid and vapor flow for the absorption process, as well as different means of removing the heat generated by the exothermic reaction.

In the first arrangement, the absorption process occurs on the outside of a tube. Thermal energy is transferred through the tube wall to fluid flowing inside the tube coil. This absorber arrangement is shown in Figure 2. The second absorber arrangement has the absorption process occurring in the tube, with the heat sink fluid on the shell-side. This arrangement is shown in Figure 3.

In the arrangement shown in Figure 2, the helical coil of tubing is enclosed in a container, and the liquid absorbent (water with a low concentration of ammonia) is discharged above the top of the tube coil by being allowed to drip out through a ring of small nozzles arranged above the coil (the feed tray with pop-rivet holes). The liquid flows down the outside of the tube in a thin film approximately 0.4 in. (1 mm) thick. In this design, the tube outside diameter is 0.625 in. (15.88 mm) in the upper part of the absorber and 0.5 in. (12.7 mm) in the lower section. As the liquid flows down the outside of the tube coil, ammonia vapor flowing upward from the bottom of the enclosing container is absorbed by the film, producing heat. The thin film results in efficient heat transfer; the thermal energy is transferred to the tube, where it is conducted through the tube wall and heats the fluid flowing inside the tube.

The geometry of interest for design of the sensor is the one shown in Figure 2. The tubing is tightly coiled so that consecutive loops of the absorber are in contact with each other, as shown in Figure 4. The liquid film is expected to remain continuous as it flows over one coil and onto the next. If the ammonia concentration sensor is to be located on the side of the absorber tube coil, it must be small enough to have no adverse impact on film flow rate and film uniformity. At a minimum, this requires that it have a profile less than 1 mm in height. The sensor for the arrangement in Figure 3 does not have such critical size constraints because there is no liquid film to disrupt. However, the sensors must not unduly disturb the flow within the tube or interfere with heat transfer through the tube wall.

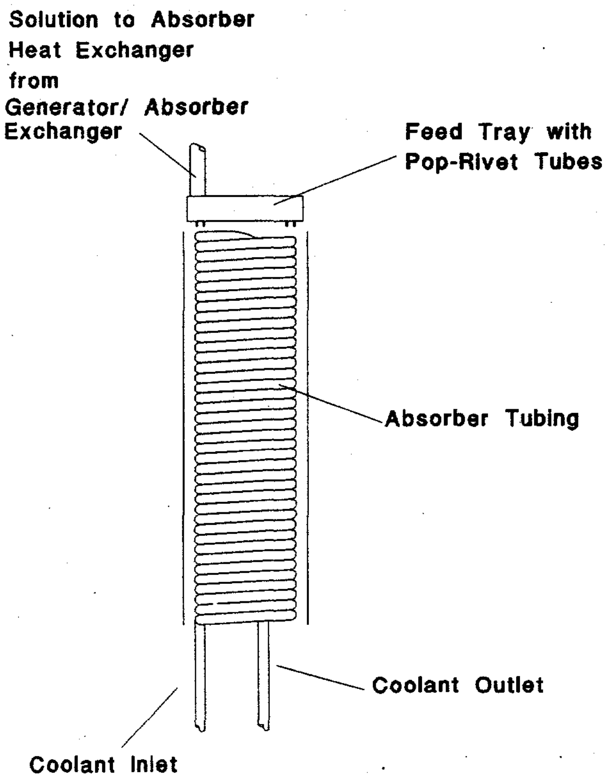

Figure 2. System Schematic

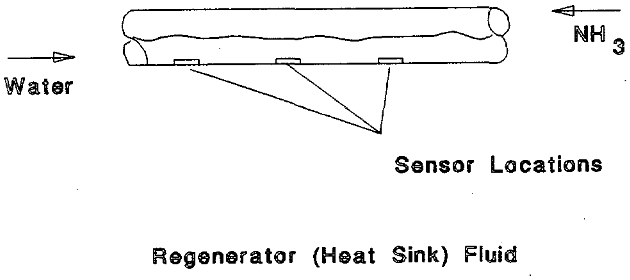

Figure 3. Tube-Side Absorber

The desirable sensor locations are shown for each arrangement in Figures 3 and 4. One sensor per tube coil will give sufficient resolution in the vertical direction for the absorber shown in Figure 4. It is also desirable to locate the sensors at different azimuthal positions around the circumference of the coil.

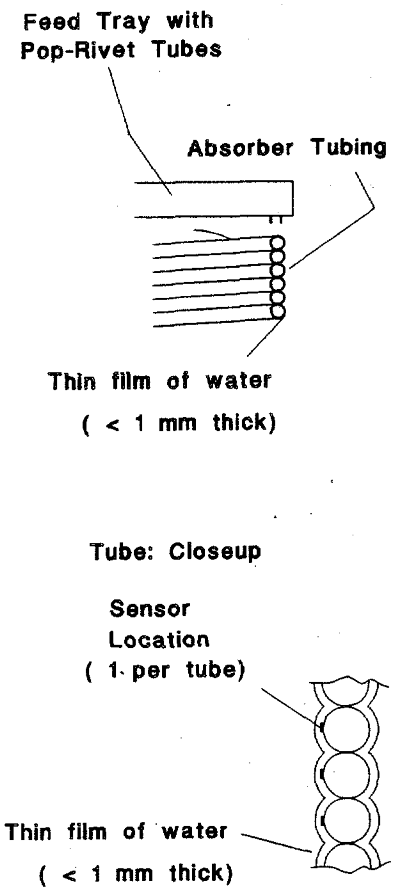

Figure 4. Tube and Film Arrangement

2.2 Material Compatibility

Material compatibility is a significant consideration in the design because of the corrosive nature of ammonia and ammonium hydroxide, which are strongly alkaline solutions.

As part of this study, PNL reviewed data for various materials from which a sensor might be constructed, looking for something that might survive the corrosive conditions in the absorber. In many cases, available data on corrosion resistance of materials did not match the range of temperatures and pressures the sensor is expected to see. Any materials actually selected for use in a sensor for this application would have to be evaluated for compatibility with ammonia and ammonium hydroxide at the operating conditions in the absorber, but the results obtained so far indicate that the choices will be extremely limited.

Rubbers and plastics seem to be relatively immune to corrosion by alkali solutions. Appendix A summarizes how a number of these responded to a solution of 28% ammonium hydroxide. Natural rubber, butyl rubber, chlorosulfonated polystyrene, chlorinated rubber, styrene rubber, neoprene, polytetrafluoroethylene, polyvinylchloride (PVC, both type I and type II), polystyrene, polyethylene, polyisobutylene, and coal tar all have a high resistance to alkali solutions. In general, they are reasonably resistant to attack at temperatures below about 100°C.

Glass laminates are unsuitable for this application, since glass is etched by ammonia and ammonium hydroxide. Ruby and sapphire crystal glass is resistant, however, and would be suitable if other material properties were acceptable. Many common sealants such as Viton and Teflon are also incompatible with ammonium hydroxide, even though, like glass, they are generally considered relatively inert. Any seals in the sensor device must be tested for compatibility with this fluid.

Metals are generally quite susceptible to attack by alkaline solutions, and it is not easy to find a suitable metal or alloy for this application.

Nickel is one metal that is unusually resistant to attack by some alkali solutions. Unfortunately, ammonium hydroxide is not one of them. It will readily form compounds with ammonium hydroxide; concentrations greater than 1% cause rapid attack of the metal. Copper has a similar susceptibility.

Stress corrosion cracking is generally greatly accelerated by the presence of an alkali solution. Copper and all copper-based alloys and brasses have a very high susceptibility to stress corrosion cracking and, therefore, would be completely unsuitable for this application. The presence of oxygen in the ammonia solution appears to be an important contributor to increased rates of stress corrosion cracking in some metals. Aluminum alloys are also rapidly corroded by ammonia and ammonium hydroxide.

The metals that appear likely to be suitable are certain alloy steels. A number of steels can be used with corrosive alkaline solutions in some applications. Mild steel does not corrode in aqueous ammonia at conditions up to 600 psi (4.134 MPa) and 930°F (499°C) and will withstand caustics in concentrations up to 50% at 150 psi (1.034 MPa). Carbon steel can be used with alkaline solutions if a sodium hydroxide corrosion inhibitor is used to coat all exposed surfaces. Ferritic stainless steels such as alloy Type 430 or the more highly alloyed Type 446 should provide the best corrosion resistance of any steel selected for this applications. Super ferritics such as 29-4C might be worth considering if metals with less alloying prove unsuitable due to excessive corrosion. However, formability of these metals is an issue that would also have to be addressed.

2.3 System Chemistry

Unlike a single-refrigerant system, such as a CFC-based system, the working fluid of an absorption machine is a hygroscopic brine—a mixture of lithium bromide and water or ammonia and water. In the BCO absorber, the working fluid is ammonia and water. Ammonia vapor is absorbed into the ammonia/water solution in an exothermic reaction that transfers the heat into the fluid flowing inside the absorber coils. In the aqueous ammonia solution, ammonia exists in equilibrium with the ammonium ion and the hydroxide ion [Equation (2.1)].

$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^- \tag{2.1}$$

The vertical length of the coil in the absorber is the primary variable affecting the overall size of the system. The falling solution film must have a path length long enough to increase the aqueous ammonia concentration from 3% to approximately 50%. As the NH_3 concentration increases from 3% to 50%, the pH of the solution is expected to increase from about 11.8 to 12.4.

The operating conditions at which the sensor must function are as follows:

- working fluid inlet conditions--
  200°F (93.3°C)
  15 to 80 psia (1.03 to 5.51 MPa)
  3% to 10% ammonia by weight[1]
- working fluid outlet conditions--
  120°F (48.9°C)
  15 to 80 psia (1.03 to 5.51 MPa)
  35% to 50% ammonia by weight
  absorber pH $\approx$ 12.

3.0 Requirements Development

The sensing techniques (or devices) reviewed were acoustic wave, refractive index, pH/colormetric, optical absorption, electrode, thermal, chemiresistor, and ion-selective field-effect transistor (ISFET) devices.

Each technique or device was evaluated against requirements, which consisted of the following parameters:

- physical constraints for *in situ* operation - size, portability, dependence on temperature, pressure, viscosity, and conductivity, material compatibility
- sensor characteristics - sensitivity, dynamic range, response time, selectivity, accuracy, reversibility, calibration
- sensor application - deployment, cost, commercially available, suitability for installation in a closed loop.

Additional constraints were applied to the requirements for the NH_3 concentration sensor, to identify both 1) an ammonia concentration measurement device for use in the BCO heat pump design and testing efforts and 2) a potential monitoring technology for use in operating commercial heat pump applications. The sensor would have to operate in the same environment in each case, but the constraints on performance would differ substantially. A laboratory instrument must be accurate, reliable, and relatively easy to install, but would not necessarily have to be very rugged, long-lived, or immune to drift. On the other hand, an instrument installed as an integral part of the control circuitry of an operating heat pump would have to be essentially indestructible, with unvarying accuracy and sensitivity over its long life span.

At this time, the laboratory sensor is the most critical because it is required to aid the design of an ammonia-absorption heat pump. The control sensor would be a valuable asset for the commercial unit, but is not absolutely necessary to the operation of the system. This priority order is fortuitous: although the laboratory application is a considerable challenge, it seems rather simple in comparison to the magnitude of the commercial sensor application, as seen from the detailed discussion of the problem presented in Section 2.

4.0 Literature Search and Review

4.1 Approach

For this study, literature searches were first performed on the Dialog information retrieval service. The key words for the first searches were *ammonia*, *ammonium hydroxide*, *solubility*, *corrosion*, and *concentration sensors*. After the relevant articles were reviewed, other searches were done with the following key words: *ammonia concentration sensors*, *chemiresistive*, *chemoptic*, *microelectronic*, *fiber optic*, *optical absorption*, *spectroscopy*, *optrode*, *integrated micro sensor*, *miniature*, *subminiature*, *solid state*, *microprobe*, and *ion selective*. Selected references cited in the initial articles were also reviewed.

The following bibliographic databases were searched:

- file 14, Ismec, mechanical references
- file 8, Compendix Plus, Engineering Index back to 1970
- file 6, NTIS, government articles and papers from national laboratories back to 1969
- file 2, Inspec, first reference for Physics and Electronics back to 1969
- file 305, Analytical Chemical Abstracts
- file 317, Chemical Engineering/Biotech/ Environmental Abstracts
- file 317, Chemical Safety Newsbase.

Books were referenced in Dialog file 470, Books in Print.

4.2 Summary of Sensor Technology

Sensing techniques reported in the open literature for determining concentrations of ammonia, ammonium, and ammonium hydroxide included mechanical, optical, electrical, thermal, and chemical detection methods. Sensing techniques for detecting mechanical properties include acoustic wave propagation. Those for sensing optical properties include measurements of refractive index and absorption. Techniques for detecting chemical properties include measurement of the pH using colormetric indicators. Electrical property sensors include chemiresistor and ISFET devices.

Many sensors employ a gas-permeable membrane to separate dissolved ammonia in the sample solution from an internal filling solution. Ammonia diffuses through the membrane and dissolves in the internal filling solution. The potential of the electrode sensing element varies in a Nernstain manner with changes in the hydroxide level. Potentiometric detection can be used to measure pH change or to directly measure the ammonium ion (which is done in the commercially available ammonia gas-sensing electrodes). One commercial gas-sensing electrode consists of a hydrophobic gas-permeable membrane separating separates the alkaline test solution from an internal solution of 0.1M ammonium chloride. When the electrode is immersed in an alkaline test solution, ammonia can diffuse across the membrane, alter the NH_3 concentration in the filling solution, and cause a pH change that is monitored by the glass electrode (Gilbert and Clay 1973; Garside et al. 1978; Merks 1975; Kaiser and Wheaton 1986; Smith and Helmuth 1975; Thomas and Booth 1973; O'Herron 1977). The membrane also prevents ionic species from entering the internal solution, thus eliminating any false response resulting from dissolved ions. However, high levels of ions can affect the solubility of ammonia to some degree. Various amperometric detection systems have also been employed. Recently, several amperometric sensors have shown selectivity to ammonium ions (Thomsen and Baldwin 1992; Osakai et al. 1987). The first sensor used electrodes coated with metal hexacyanoferrate, and the other used a poly(vinyl chloride)-nitrobenzene gel electrode containing dibenza-18-crown-6 for selectivity to ammonium ions.

Infrared spectroscopy is one of the most prevailing means of detecting or analyzing gaseous molecules. Planar waveguide and fiber optic evanescent sensors have been used to identify ammonia vapors by measuring their spectral signature (Giuliani et al. 1984; Sanghera et al. 1994). The portion of light penetrating a small distance into the waveguide cladding during every reflection at the core/cladding boundary, called evanescent wave, can be spectrally absorbed by molecules of the surrounding medium. Researchers have also used other spectroscopic methods with lasers and remote absorption cells to observe the fundamental infrared or overtone near-infrared absorption lines of ammonia vapor with detection limits near 1 ppm (Simhony and Katzir 1985; Meinburg et al. 1990; Feher et al. 1993). A common technique for improving the sensitivity of detection is through preconcentration of the species on a matrix that does not interfere during analysis (Ataman and Mark 1977).

To ascertain vapor-phase ammonia, optical waveguides have been coated or doped with a variety of pH/colormetric indicators (Guiliani et al. 1983; Shahriari et al. 1988; Blyler et al. 1989; Muto et al. 1989; Tabacco et al. 1992; West et al. 1992; Sadaoka et al. 1992; Golubkov et al. 1992; Klein and Voges 1993). Similar sensors have been developed for detecting aqueous ammonia (Arnold and Ostler 1986; Dickert et al. 1989; Kawabata et al. 1990; Reichert et al. 1990; Sellien et al. 1992). Reaction between the indicator and the ammonia results in an absorption of the light passing through the waveguide, and the degree of light absorption is related to the ammonia concentration. The indicator is immobilized into a polymer matrix such as silicone rubber, polymethylmethacrylate, or polyvinyl alcohol or onto glass and is phase-separated using a gas-permeable membrane. In aqueous solutions, the ammonium ion is in equilibrium with ammonia. Diffusion of ammonia into the membrane deprotonates the pH-indicator. This deprotonation by the ammonia varies according to the concentration of ammonium ions in the solution and can be detected spectroscopically by observing the indicator color change. Typical colormetric indicators include Bromophenyl Blue (BPB), p-Xylenol Blue (PXB), Bromocresol Green (BCG) and Bromocresol Purple (BCP), p-nitrophenol, dodecyl-acridine orange (dodecyl-AO$^+$), Reichardt's dye, indophenol, triphenylmethane dye, tymolblue (TB) dye, and oxazine 750 perchlorate dye. One of the problems encountered with conventional evanescent absorption sensors is their characteristic low sensitivity, resulting from the limited depth of penetration of the evanescent field into the indicator. The use of porous optical fibers, doped with colormetric indicators, has shown improved sensitivity over evanescent sensor for in-line optical absorption measurements (Shahriari et al. 1988; Tabacco et al. 1992).

Thermal ($LiTaO_3$) sensors combined with an acid membrane have been used to detect low concentrations of ammonia vapor (D'Amico et al. 1993). The pyroelectric sensor detects the heat resulting from an ammonia-acid membrane interaction. The sensor suffers interferences from spurious heat, pressure, and turbulence sources.

A refractive index sensor with glass optical fibers has been used to determine real-time concentrations of lithium bromide along the heat exchange tubes of an absorber vessel (Bostick et al.

1986; Klatt et al. 1987). This technique is limited to binary mixtures with a refractive index just slightly lower than the fiber core. Temperature compensation must be carefully performed to obtain reliable concentration readings. Furthermore, corrosion of bare glass fibers becomes a major issue in alkaline solutions.

Acoustic wave devices for detecting chemical compounds have been used primarily as gas phase gravimetric sensors (Ali et al. 1992). The use of acoustic wave sensors in liquid medium is questionable because their oscillations are seriously affected by viscous damping and conductivity. Many researchers have compensated for these undesirable effects by applying theoretical or empirical corrections to the sensor output signal (Wei et al. 1991, 1992; Hayward 1992; Duncan-Hewitt and Thompson 1992; Barnes et al. 1992; Yang and Thompson 1993; Shen et al. 1993; Cavic-Vlasak and Rajakovic 1992). The results of these methods have shown some promise but are limited to narrow bounds of operation. Metal films have been used to shield the sensor from loss resulting from electrical dissipation into the fluid, but the sensitivity remains limited by viscous damping (Baer and Flory 1991). Using a differential measurement technique and high resonant frequencies, Dunham et al. (1995) have demonstrated reliable and sensitive acoustic wave measurements in liquids.

The electrical properties of many organic films are significantly affected by chemisorption of ammonia vapors. The sensitivity to adsorbed impurities is an important factor in the use of these films as gas-phase chemical sensors. A chemiresistor sensor is fabricated from a very thin organic semiconductor film deposited onto a planar microelectrode array. Ammonia vapors interacting with the semiconductor produce current changes under constant voltage bias conditions (Wohltien et al. 1985; Brina et al. 1990). A ratiometric measurement scheme provides temperature compensation and scaled voltage output proportional to the conductance change in the sensor. Phthalocyanine thin films are particularly useful because of their chemical and thermal stability. These sensors respond to ammonia vapor at ambient temperatures; the effect of relative humidity is substantial.

Microelectronic ion sensors based on monolithic silicon integrated circuit technologies have been the subject of considerable research and development for more than 20 years (Kelly and Owen 1985). ISFET ammonia and ammonium sensors based on the changes in electrical properties of metal oxide semiconductor devices have been described by Oesch et al. (1981), Peschke et al. (1990), and Popova et al. (1994). Oesch et al. (1981) demonstrated the direct measurement of the ammonium ion (NH_4^+) in aqueous solutions. The ISFET sensor forms a microminiature, differential ion-measuring probe, suitable for *in situ* measurements. Peschke et al. (1990) achieved response times on the order of seconds near ambient temperatures. ISFETs can suffer from problems associated with thermal instability, output drift, and encapsulation. Deployment in aqueous-phase solutions has been found to shorten sensor lifetime because of water seepage between the polymer membrane and the epoxy wall (Oesch et al. 1981).

5.0 Conclusions and Recommendation

Based on the results of this study, several conclusions can be drawn regarding the suitability of existing sensors for ammonia and ammonium hydroxide detection. Those conclusions and our overall recommendation are given in this section.

5.1 Conclusions

Numerous chemical sensors for detecting ammonia in vapor phase and aqueous solutions have been reported in the literature. Most of the sensors described were useful only for vapor-phase detection and lacked selectivity to the ammonium ion. In the ammonia/water absorption cycle, ammonium concentrations range from approximately 3% to 50%. Most of the technologies we reviewed had detection limits at the parts-per-million or parts-per-billion level, with limited dynamic range. In addition, most of the sensor evaluations were performed at ambient temperature and pressure and at constant relative humidity. Their performance in the ammonia absorption cycle environment is questionable.

General problems with these sensors include insufficient selectivity (e.g., response to nontarget compounds; humidity); the lack of adaptability to microminiaturization; limited dynamic range; long response time; irreversibility; and inability to withstand the temperatures, pressures, and chemically corrosive environments encountered within absorption cycle machines.

The required selectivity of the monitoring system for ammonium hydroxide is complicated by the presence of high concentrations of both water vapor and ammonia vapor in the absorber chamber and in the falling solution film. Furthermore, the sensing element used to monitor ammonium hydroxide concentrations must be constructed of a material that can survive contact with the solution, which is characterized by pH values up to 12.4. The sensors must also be sufficiently small to prevent significant perturbations to the flow of the aqueous film across the absorber coil. Disturbing the film could have adverse effects on the rate of absorption of NH_3 or cause perturbations that distort the local concentration enough to give biased or unreliable readings.

5.2 Recommendation

Information obtained in the literature search leads us to recommend that follow-up activities focus on ISFET devices and a fiber optic evanescent sensor with a colormetric indicator. The ISFET and fiber optic evanescent sensor are inherently microminiature and capable of *in situ* measurements. Further, both techniques have demonstrated selectivity for the ammonium ion (NH_4^+). The primary issue that remains is whether each can be made corrosion-resistant without creating a negative impact on system performance.

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Appendix A

Compatibility of Plastics and Polymers

Appendix A

Compatibility of Plastics and Polymers

The following tests were done with 28% ammonium hydroxide.

Chlorinated rubber is not attacked in the range of 75°F (23.9°C) to 125°F (51.7°C).

Styrene Butadiene Copolymer is not attacked from 75°F (23.9°C) to 150°F (65.6°C).

Neoprene is not attacked in the range of 75°F (23.9°C) to 160°F (71.1°C).

Epoxy (type unknown) is not attacked in the range of 75°F (23.9°C) to 200°F (93.3°C).

Plasticized PVC is not appreciably attacked in the from 75°F (23.9°C) to 150°F (65.6°C).

Furan Resin Cement (a liner) is not attacked from 75°F (23.9°C) to 250°F (121.1°C).

Impervious Graphite is not attacked from 75°F (23.9°C) to 300°F (148.8°C).

Polyethylene is not attacked from 75°F (23.9°C) to 125°F (51.7°C).

PVC type I is not attacked from 75°F (23.9°C) to 160°F (71.1°C).

PVC type II is not attacked from 75°F (23.9°C) to 150°F (65.6°C).

Polutetrafluoroethylene is not attacked from 75°F (23.9°C) to 250°F (121.1°C).

Chlorinated polyether (Penton) is attacked to 28% at 221°F (105°C).

Appendix B

Sensor Matrix

Appendix B

Sensor Matrix

In this appendix, two aspects of the sensor study are documented in tabular form. Table B.1 is a matrix of sensor references. In Table B.2, a matrix displays the specifications for each sensor evaluated in this study.

Table B.1. Reference Matrix

Sensing Technique	Author/ Organization	Title	Keywords	Citation	Sensor Type	Ref #	Other	Abstract	Comments
Acoustic Wave	Yang, Mengsu; Thompson, Michael – Dept. of Chem., U. of Toronto	Multiple Chemical Information from the Thickness Shear Mode Acoustic Wave Sensor In the Liquid Phase	shear mode, acoustic wave sensor, multiple chemicals	Analytical Chemistry, 1993, vol 65, pp 1158-1168	TSM Acoustic Wave	1		Effects of viscosity, density, and dielectric constant on the response of a TSM bulk acoustic wave sensor examined w / respect to frequency response and electrical properties of the circuit involved.	Theory, No ammonium detection
Acoustic Wave	Cavic-Vlasak, Biljana A; Rajakovi, L. Jubinka V. – Dept of Anal. Chem., Faculty of Technology and Metallurgy, U. of Belgrade, Yugoslavia	Application potential of liquid-phase acoustic wave devices as chemical and biochemical sensors.	liquid-phase acoustic wave device, chemical and biochemical sensors	Fresenius J. Anal. Chem., 1992, vol 343, pp 339-347	bulk acoustic wave	2		Potential of BAW as liquid-phase sensor evaluated with regard to sens. of sensor to liquid medium properties and device's liquid-solid interface. Surface free energy and interfacial visc. have sig. influence on freq. response.	Discussion of liquid-phase acoustic wave devices. No ammonium detection.
Acoustic Wave	Duncan-Hewitt, Wendy C. – Faculty of Pharm., U. of Toronto. Thompson, Michael – Dept. Chem., U. of Toronto	Four-Layer Theory for the Acoustic Shear Wave Sensor in Liquids Incorporating Interfacial Slip and Liquid Structure	shear wave sensor, interfacial slip liquids, theory	Anal. Chem., vol 65, no. 1, Jan 1, 1992, pp 94-105	acoustic shear wave	3		Theory describes behavior of thickness shear mode acoustic wave sensors in liquids, allowing for introduction of solid sensor, surface-adjacent liquid, transition, and bulk liquid layers. Calculations given for series freq. resp., impedance, phase	Theory, No ammonium detection
Acoustic Wave	Wei, Wanzhi; Mo, Zhihong; Yao, Shouzhou – Dept. Chem. & Chem.E., Human U., Changsha, China	Multi-component analysis in solution using piezoelectric quartz sensors.	multi-component, piezoelectric sensors, cresol in water	Analytica Chimica Acta, vol 251, 1991, pp 143-148	quartz piezoelectric crystal	4		Four piezo quartz crystals working at different pH levels used to determin o- and m- cresol in H20. Average prediction errors were 10% and 4.8% with MLR and 5.2% and 3.4% with PLS stat. analysis.	Theory, No ammonium detection
Acoustic Wave	Wei, Wanzhi; Nie, Lihua; Yao, Shouzhou – Dept. Chem & Chem.E., Human U., Changsha, China	Multi-component anaylysis in solution using piezoelectric quartz sensors.	piezoelectric quartz sensors, analysis in water, multiple components	Analytica Chimica Acta, vol 263, 1992, pp 77-83	quartz piezoelectric crystal	5		Detection of simple organic acids in water. Linear dependence upon concentration. Calibration model established. Average relative errors: 0.81% for asprin, 1.63% for salicylic acid.	Theory, No ammonium detection
Acoustic Wave	Hayward, Gordon – School of Engineering, U. of Guelph, Guelph, Ontario, Canada	Viscous interaction with oscillating piezoelectric quartz crystals.	piezoelectric sensors, quartz . crystals	Analytica Chimica Acta, vol 264, 1992, pp 23-30	quartz piezoelectric crystal	6		Model: relates equiv. circuit. params of quartz crystal to the viscous energy dissipation developed from solution of Stokes' second problem & compared to experimental data. Surface oscillation amplitude approx. 2E-12 meters. Alt. model. apprch. suggested	Theory, No ammonium detection
Acoustic Wave	Ali, Zulfiqur; Thomas, CL Paul; Alder, John F – Dept of Inst. & Anal. Sci., UMIST, Manchester, UK and Marshall, Geoffrey B. – Nat. Power. Tech. & Env. Centre, Leatherhead, Surrey, UK	Denuder Tube Preconcentration and Detection of Gaseous Ammonia Using a Coated Quartz Piezoelectric Crystal.	ammonia, piezoelectric crystal, denuder tube, preconcentration	Analyst, May 1992, Vol 117, pp 899-903	coated quartz piezoelectric crystal	7		Using denuder tube for sampling gaseous ammonia; detection with piezo quartz crystal. Tube coated w/ tungsten oxide; crystal w/ pyridoxine hydrochloride. 29 ng/l of ammonia in air detected w/ signal to background ratio of 14:1 w/ enrichment ratio of 900	Gas-phase detection

Table B.1. Reference Matrix

Sensing Technique	Author/ Organization	Title	Keywords	Citation	Sensor Type	Ref #	Other	Abstract	Comments
Acoustic Wave	Dunham, Glen C.; Benson, Nicholas H; Petelenz, Danuta; Janata, Jiri – Molecular Science Research Center, PNL	Dual Quartz Crystal Microbalance	piezoelectric sensors, quartz crystals	Report originating from PNL	quartz piezoelectric crystal	8		Dual quartz crystal microbalance probe developed that is operable in gaes and conducting or viscous liquids. Sensitivity to added mass is df/dm = 0.23 Hz/ng.	Discussion of liquid-phase acoustic wave devices. No ammonium detection.
Acoustic Wave	Shen, D.Z.; Zhu, W.H.; Nie, L.H.; Yao, S.Z. – New Materials Research Institute, Human University, Changsha, China	Behaviour of a series piezoelectric sensor in electrolyte solution.	piezoelectric, sensor, electrolyte, solution, behavior, conductimetry, oscillometry	Analytica Chimica Acta, Vol. 276, 1993, pp 87-97	piezolectric	9		Theory, methodology, behavior of piezoelectric and conductivity sensors in electrolyte solution. Sensor construction: At-cut piezo qtz. crystal conn. in series w/ conductivity electrode. Effects of physical property changes in solution.	Theory, No ammonium detection
Acoustic Wave	Barnes, C.; D'Silva, C.; Jones, J.P.; Lewis, T.J. – School of Electronic Engineering Science, U. of Wales Bangor, Dean Street, Bangor, Gwynedd, UK	The theory of operation of piezoelectric quartz crystal sensors for biochemical application	piezoelectric quartz crystal sensors, biochemical, theory,	Sensors and Actuators A, vol 31 (1992), pp 159-163	piezoelectric	10		Piezolectric quartz crystal detects binding of analyte by means of sensor layer attached to crystal. This paper discusses the theory of operation of such sensor.	Theory, No ammonium detection
Acoustic Wave	Baer, Richard L.; Flory, Curt A. – Hewlett-Packard Laboratories, Palo Alto, CA	Some Limitations on the Use of Leaky Saw Mode Sensor in Liquids	limitations, leaky SAW mode sensors, liquids	1991, Ultrasonic Symposium, pp. 279-284	SAW sensors	11		SAW sensors suffer attenuation when immersed in liquids. Most significant loss for unshielded LSAW is electrical dissipation, induced by conductivities and dielectric loss tangents of many fluids. Shielding sensor w/ metal film eliminates loss.	Discussion of liquid-phase acoustic wave devices. No ammonium detection.
Refractive Index	Klatt, LN; Bostick, DT – Anal. Chem. Div. ORNL, and Perez-Blanco, H – Energy Div., ORNL	The fiber-optic refrigeration cycle monitor.	fiber optic, refrigeration, absorption	SPIE, vol. 787, Optical Techniques for Sensing and Measurement in Hostile Environments, 1987, p. 2-7	fiber optic refractometer	12		Fiber optic sensor inserted into refrigerant absorption fluid at user-definable points to make real-time measurements of fluid's refractive index. Thermocouple also used. Temperature and concentration measurements enable in-line monitoring and control.	lithium bromide detection only
Refractive Index	Bostick. D.T.; Klatt, LN;Strain J.E.; Perez-Blanco H – Anal. Chem. Div. ORNL, and Energy Div., ORNL	Real-time in-situ refractometer for concentration measurements in absorption machines	fiber optic, refrigeration, absorption	ASHRAE V. 92, Pt. 2, 1986	fiber optic refractometer	13		Fiber optic sensor inserted into refrigerant absorption fluid at user-definable points to make real-time measurements of fluid's refractive index. Thermocouple also used. Temperature and concentration measurements enable in-line monitoring and control.	lithium bromide detection only
Refractive Index	Bolarski, AA; Ridgway, RW; Busch, JR; Turhan-Sayan, G; Miller, LS – Battelle Memorial Institute, Columbus, OH	Integrated Optic Biosensor for Environmental Monitoring	integrated-optic, biosensor, liquid pollutant	SPIE, Vol. 1587, Chemical, Biochemical, and Environmental Fiber Sensors III (1991)	waveguide Mach-Zehnder interferometer	14		Mach-Zehnder interferometer structure used to measure thickness and/or refractive index changes on the waveguide surface, to monitor the concentration of liquid pollutants on the surface of a planar substrate. PPM levels of detection: PPB possible, too.	No ammonium detection

Table B.1. Reference Matrix

Sensing Technique	Author/ Organization	Title	Keywords	Citation	Sensor Type	Ref #	Other	Abstract	Comments
Electrode	Karsten, T. N.; Baldwin, R.P./University of Louisville	Evaluation of Electrodes Coated with Metal Hexacyanoferrate as Amperometric Sensors for Nonelectroactive Cations in Flow Systems	amperometric ammonium-ion electrode, nonelectroactive cation detection	Electroanalysis 2 (1990) 263-271	amperometric electrode	15		Electrode coated with hexacyanoferratic films to detect nonelectroactive cations in a flow-injection system. This electrode responded to NH4+ ions with detection limits of 0.2µM and 2 orders of linear response.	ammonium-ion electrode
Electrode	Kaiser, G. E; Wheaton, F. W.; Univ of Maryland	Automation of Water Quality Measurements for Aquaculture Systems	aquaculture engineering, water quality, ammonia measurement, instrumentation	presented at the American Society of Aquacultural Engineers, June 29 July 2, 1986	potentiometric gas-sensing electrode, Orion Ammonia Electrode Model 95-10	16		Ammonia measurements were automated using a computer and an Orion Ammonia Electrode Model 95-10.	NH3 sensor only
Electrode	Merks, A. G. A.; Delta Instit. Hydrobio. Res.	Determination of Ammonia in Sea Water with an Ion-Selective Electrode	solid-state, ammonia gas-sensing electrode	Netherlands Journal of Sea Research 9 (3-4): 371-375 (1975)	potentiometric gas-sensing electrode, Orion Ammonia. Electrode Model 95-10	17		An Orion Ammonia Electrode Model 95-10 was used to determine levels of ammonia in sea water between 0.1 and 2.0 mg/l	NH3 sensor only
Electrode	O'Herron, R.J./US EPA Cincinnati, Ohio	Investigation of the Orion Rearch Ammonia Monitor	ammonia electrode, sea water, multilayered gas diffusion membrane.	EPA-600/4-77-028	multilayered gas diffusion membrane w/ Orion Ammonia Electrode Model 95-10	18		An Orion Ammonia Electrode Model 95-10 was investigated by the EPA.	NH3 sensor only
Electrode	Thomas,R. F; Booth, R. L./US EPA Cincinnati, Ohio	Selective Electrode Measurement of Ammonia in Water and Wastes	ammonia electrode, sea water, multilayered gas diffusion membrane.	Environ. Sci. Technol. 7: 523-526	multilayered gas diffusion membrane w/ Orion Ammonia Electrode Model 95-10	19		An Orion Ammonia Electrode Model 95-10 was used to determine levels of ammonia in sea water and waste . Its' performance was compared to those from the indophenol blue method.	NH3 sensor only
Electrode	Gilbert, Thomas R; Clay, Alice M./The New England Aquarium, Boston, MA 02110	Determination of Ammonia in Aquaria and Sea Water Using the Ammonia Electrode	ammonia electrode, sea water, multilayered gas diffusion membrane.	Analytical Chemistry, Vol. 45, No. 9, pp 1757-58, 1973	multilayered gas diffusion membrane w/ Orion Ammonia Electrode Model 95-10	20		An Orion Ammonia Electrode Model 95-10 was used to determine levels of ammonia in sea water . Analysis below 10 ppb had longer equilibration time.	NH3 sensor only
Electrode	Garside, Christopher, Hull Gretchen, Murray Susan /Bigelow Lab for Ocean Sciences	Determination of submicromolar concentrations of ammonia in natural waters by standard addition method using a gas-sensing electrode	solid-state, ammonia gas-sensing electrode	Limnol. Oceanogr., 23(5), 1978, 1073-1076	potentiometric gas-sensing electrode, Orion Ammonia Electrode Model 95-10	21		The electrode senses change in pH of an internal NH4OH-chloride solution. The electrode is a commercially available Orion Research model 95-10. Requires 150 ml sample size.	NH3 sensor only
Electrode	Smith, Maurice L; Hellmuth, EW – Dept. of Chem., U. of Missouri-KC	Ammonia Transport in Water Saturated Polymeric Films	ammonia, water, polymeric films, gases, permeability	? - report	glass electrode	22		An examination of the theory behind ammonia transport in water saturated polymeric films.	NH3 sensor only

Table B.1. Reference Matrix

Sensing Technique	Author/ Organization	Title	Keywords	Citation	Sensor Type	Ref #	Other	Abstract	Comments
Electrode	Osakai, Toshiyuki; Senda, Mitsugi/ Kyoto U., Kyoto Japan AND Kakutani, Tadasaki / Kyoto U., Kyoto, Japan	A Novel Amperometric Ammonia Sensor	amperometric ammonium-ion sensor, PVC-nitrobenzene gel electrode	Analytical Sciences, December 1987, Vol. 3	amperometric	23		Amperometric ammonium-ion selective PVL-nitrobenzene gel elcetrode containing dibenza 18-crown-6 was covered w/ gas permeable membrane. Sensor gave current response proportional to the ammonia concentration from 2 to 200 micromol/cubic dm.	ammonium-ion electrode
Thermal	D'Amico, A., Faccio, M., Ferri, G., Ponti, P.P., Savelli, G., and Spreti, N. /University Tor Vergata	Low concentration ammonia detection by LiTaO3	pyroelectric sensor, LiTaO3, acid membranes	Sensors and Actuators B, 13-14 (1993) 148-150	pyroelectric-thermal	24		Two different acid membranes used on pyroelectric sensor: nonanoic and ethanesulfonic acid. Signals result from heat due to NH3-acid membrane interaction.	NH3 sensor only, suffers pressure and temperature interferences
Chem-FET	Popova, LI; Andreev, SK; Gueorguiev, VK; Stoyanov, ND – Inste. of Solid State Physics, Bulgarian Acad. Sci., Sofia, Bulgaria	Voltage dependence of gas-sensing behaviour of SnO2-gate FET's	SnO2 gate FET, gas-sensing, voltage dependence	Sensors and Actuators B., vol 18-19 (1994), p 543-545	SnO2 gate FET	25		Investigation of SnO2 gate FET's at constant ammonia concentration (100 ppm) and different bias conditions.	
Chem-FET	Oesch, Urs; Caras, Steve; Janata, Jiri – *Dept. Bioengineering,* U. of U., SLC, Utah	Field Effect Transistors *Sensitive to Sodium and* Ammonium Ions	FET, sodium and ammonium ions, ion-selective	Analytical Chemistry, 1981, *vol. 53, pp 1983-* 1986	ISFET	26		New ISFET (Ion-Selective Field Effect Transistor) for Na+ and NH4+ presented. Selectivity and sensitivity are coincident to *the corresponding potentiometric ion-*selective electrodes	
Chem-FET	Bezegh, Kara; Bezegh, Andras; Janata, Jiri / U. of U., SLC, Utah and Oesch, Urs; Xu, Alping, Simon, Wilhelm/ Swiss Fed. Instte. Tech., Zurich, Switzerland	Multisensing Ion-Selective Field-Effect Transistors Prepared by Ionophore Doping Technique	ion-selective, FET, ionophore doping	Analytical Chemistry, 1987, vol. 59, 2486-2488	ISFET	27		Improved procedure for prep. of multi-gate ISFETs w/ polymeric membranes. Main benefit: membrane is continuous, mechanically stable and w/o elec. shunts between membrane and encapsulant.	
Chem-FET	Bezegh, Klara; Petelenz, Danuta; Bezegh, Andras; Janata, Jiri – Dept. of Bioengineering, U. of U., SLC, Utah	Integrated Solid State Probe for Determination of Activity of Sodium Chloride	ISFET, solid state probe, sodium chloride	Analytical Chemistry, 1987, vol 59, pp 1423-25	ISFET	28		Dual ISFET probe prepared by applying Na+ and Cl- selective membranes to adjacent gates of same transistor chip. More stable than individual ISFETs. Tested in the range of 10E-4 to 1 M NaCl.	
Chem-FET	M. Peschke, H.; Lorenz, H; Riess, H. Eisele, I./Universitat der Bundeswehr	Recognition of Hydrogen and Ammonia by Modified Gate Metallization of the Suspended-Gate FET	SGFET, solid state probe, hydrogen, ammonia	Sensors and Actuators, B1 (1990) 21-24.	SGFET	29		Suspended-gate FET were used to detect ammonia in synthetic air. The suspended-gate was modified by deposition of SnOx.	
Electrical Conductivity	Vigmond, Stephen J.; Kallury, Krishna MR; Ghaemmmaghami, Vida; Thompson, Michael – Dept. of Chem., U. of Toronto, Toronto, Ontario, Canada	Characterization of the Polypyrrole Film-Piezoelectric Sensor Combination	polypyrrole film, piezoelectric sensor, TSM acoustic waves	Talanta, vol 39, no. 4, pp 449-456, 1992	piezoelectric, coated	30		TSM acoustic wave sensors coated with polymerizd pyrrole by electrochem. methods. Films characterized w/ scanning electron microscope. Freq. decreases for sensors exposed to methanol, toluene, and ammonia evaluated.	

Table B.1. Reference Matrix

Sensing Technique	Author/ Organization	Title	Keywords	Citation	Sensor Type	Ref #	Other	Abstract	Comments
Electrical Conductivity	Brina, Rossella; Collins, Greg e; Lee, Paul A; Armstrong, Neal R – Dept. of Chem., U. of Az., Tucson, AZ	Chemiresistor Gas Sensors Based on Photoconductivity Changes in Phthalocyanine Thin Films: Enhancement of Response toward Ammonia by Photoelectrochemical Deposition with Metal Modifiers	pthalocyanine thin films, chemiresistor, ammonia, metal modifiers	Analytical Chemistry, 1990, vol 62, pp 2357-2365	chemiresistor gas sensor	31		Determination of NH3 in flowing N2 or air demonstrated by monitoring changes in photoconductivity of chloroindium phthalocyanine (InPc-Cl) and chlorogallium phthalocyanine thin films deposited of platinum silicide microcircuits. Response: 1.5 to 5.4 ppm	
Electrical Conductivity	Wohltjen, Hank; Barger, William R; Snow, Arthur W.; Jarvis, Lynn N.	A Vapor-Sensitive Chemiresistor Fabricated with Planar Microelectrodes and a Langmuir-Blodgett Organic Semiconductor Film	chemiresistor, vapor-sensitive, organic semiconductor film, planar microelectrodes	IEEE Transactions on Electrical Devices, Vol ED-32, No. 7, July 1985, pp 1170-1174	chemiresistor	32		Vapor-sensing method developed is compatible w/ monolithic silicon microelectronics tech. Elec. conduct. changes caused by vapor interact. w/ very thin films of organic semiconductors are shown to be sensitive, reproducible, rapid, and stable detectors.	
pH/Colormetric	Reichert, J; Sellien, W; Ache, HJ – Institut fur Radiochemie, Karlsruhe, Germany	Development of a Fiber-optic Sensor for the Detection of Ammonum in Environmental Waters	fiber-optic, ammonium, water, bromophenol blue	Sensors and Actuators A, 25 27, 1991, pp 481-482	fiber optic	33		Fiber-optic sensor for monitoring the ammonium content in aqueous solutions. Plastic fibers used. Sensor's sensitivity, response time, etc. similar to that of ion-selective electrodes. Bromophenol blue as indicator dye.	
pH/Colormetric	Sellien, W; Czolk, R; Reichert, J; Ache, HJ – Institut fur Radiochemie, Karlsruhe, Germany	Development of an optical-chemical sensor for the development of ammonium ions	ammonium, aqueous solutions, pH, p-Xylenol Blue, bromophenol blue	Anal. Chim. Acta, vol 269, 1992, pp 83-88	optical	34		Optical chemical sensor based on immobilized pH indicator. Detection limit: 1E-6 mol/l NH4+. Response time ranges from 1 to 60 min. Long term stability better than 6 months. p-Xylenol blue, bromophenol blue	
pH/Colormetric	Arnold, Mark A; Ostler, Tiffany J – Dept. Chem., U. of Iowa	Fiber Optic Ammonia Gas Sensing Probe	pH, fiber optic, ammonia, aqueous solutions, p-nitrophenol	Analytical Chemistry, 1986, vol. 58, pp 1137-1140	fiber optic	35		Fiber optic ammonia gas sensing probe in which the pH indicator dye p-nitrophenol is employed. Ammonia measurements in aqueous solutions are demonstrated with lower detection limit of 0.5 microMolar. p-nitrophenol used as indicator dye.	
pH/Colormetric	Emerson, Kenneth; Russo, Rosemarie C.; Lund, Richard E.; Thurston, Robert V. / Montana State U., Bozeman, MT	Aqueous Ammonia Equilibrium Calculations: Effect of pH and Temperature.	pH, ammonia, aqueous solutions, equilibrium	Journal on the Fisheries Research Board of Canada, vol 32, no. 12, Dec 1975, pp. 2379-2383	n/a	36		Study of equilibrium of ammonia in aqueous solutions based on changes in pH and temperature.	

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Sensing Technique	Author/ Organization	Title	Keywords	Citation	Sensor Type	Ref #	Other	Abstract	Comments
pH/Colormetric	Hickel, B – DSM/DRECAM/SCM URA 331 CNRS CE SACLAY, 91191 Gif sur Yvette Cedex, France and Sehested, K. – Riso National Laboratory, DK 4000 Roskilde, Denmark	Reaction of Hydroxyl Radicals with Ammonia in Liquid Water at Elevated Temperatures.	hydroxyl radicals, ammonia, liquid water, elevated temperatures	Rdiat. Phys. Chem., vol. 39, no. 4, pp. 335-357, 1992	radiolysis	37		Reaction of hydroxyl radical with ammonia in aqueous solutions has be studied by pulse radiolysis in temperature range of 20-200° C.	
pH/Colormetric	Kawabata, Yuji; Kamichika, Toshito; Imasaka, Totaro; Ishibashi, Nobuhiko – Faculty of Engineering, Kyushu University, Hakozaki, Fukuoka, 812, Japan	Ion-Selective Optrode Using Hexaydecyl-Acridine Orange Attached on Poly(vinyl chloride) Membrane	ion-selective, pH, hexadecyl acridine orange, PVC membrane	Analytical Chemistry, 1990, vol. 62, pp 2054-2055	potassium ion optrode	38		Potassium ion optrode using dodecyl-acridine orange attached to PVC membrane. Hexadecyl-acridine orange also used.	
pH/Colormetric	Reichert, J; Sellien, W; Ache, HJ – Institut fur Radiochemie, Karlsruhe, Germany	An optical ammonium-sensor for the analysis of environmental waters	ammonium, waters, optical	Fresenius J. Anal. Chem., 1991, vol 339, p. 467	optical -coated glass rod	39		Optical sensor developed for monitoring ammonim content in environ. waters. Sensor based on glass rod coated w/ caoutchouc layer in which bromophenol blue was immobilized as indicator. Detection limit of 3 micromoles/l of ammonium was obtained.	
pH/Colormetric	West, Steven J; Ozawa, Satoshi; Seiler, Kurt; Tan , Susei SS; Simon, Wilhelm – Dept. Organic Chem., Swiss Federal Inst. of Tech., Zurich, Switzerland	Selective Ionophore-Based Optical Sensors for Ammonia Measurements in Air	ionophore, ammonia, air, selective	Analytical Chemistry, vol. 64,no. 5, March 1992, pp 533-540	ion selective chromophore	40		Optodes based on the incorporation of ammonium ion-selective ionophores and hydrogen ion-selective chromoionphores in plasticized PVC membranes applied to measurement of ammonia in air. 0.002 to 100 ppm, and response times from 230 s to 15 s.	
pH/Colormetric	Sadaoka, Yoshihiko; Sakai, Yoshiro; Murata, Yu-uki – Dept. Appl. Chem., Fac. of Eng., Ehime U., Matsuyama, 790, Japan	Optical Humidity and Ammonia Gas Sensors using Reichardt's Dye-Polymer Composites	ammonia, gas sensors, dye-polymer composites, Reichardt's betain dye	Talanta, vol 39, no 12, pp 1675-1679, 1992	dye-polymer	41		Optical intensity reflected at 590 nm by Reichardt's betain dye-polymer composites treated with HCl decreased w/ an increase of ammonia concentration, and sensitivity enhanced with presence of H2O vapor.	
pH/Colormetric	Golubkov, SP; Vasilenko, NA; Potyrailo, RA; Kovtun, VS; Borsuk, PS – Kiev Polytechnic Institute, Kiev, Ukraine	Application of pH dyes for ammonia sensing by portable analyzer.	pH dye, ammonia, portable analyzer, Bromocresol Purple	SPIE vol 1637, Env. and Process Mon. Tech., 1992, pp 227-232	dye-film/optical	42		Portable device, continuously measures ammonia gas concentrations. Detection based on reversible changes in optical transmittance of dye-film coated on glass support. Bromocresol purple used as indicator dye.	
pH/Colormetric	Gulliani, JF; Wohltjen, H; Jarvis, NL – Chem. Division, US Naval Research Lab, Washington DC	Reversible optical waveguide sensor for ammonia vapors	oxazine perchlorate dye, reversible, reflectance, ammonia gas	Optics Letters, vol. 8, no. 1, Jan. 1983, pp. 54-6	waveguide absorbance measurement via pH/colormetric dye	43		Small glass capillary tube fitted with LED and photoresistor detector to form multiple reflecting optical waveguide device. Capillary coated w/ oxazine pherchlorate dye demonstrated capability of reversible sensing of ammonia vapors. 60 to 1000 ppm	

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Sensing Technique	Author/ Organization	Title	Keywords	Citation	Sensor Type	Ref #	Other	Abstract	Comments
pH/Colormetric	Shahriari, Mahmoud R.; Sigel, George H. Jr.; Zhou, Quan – Rutgers U., Fiber Optics Mat. Research. Program, Piscataway, NJ	Porous glass fibers for high sensitivity chemical and biological sensors.	glass fibers, chemical, biomdedical, sensors, gases, liquids, low concentrations	SPIE, vol. 838, Fiber Optic and Laser Sensors V (1987)	porous fiber optic pH/colormetric	44		Porous optical fiber developed for use as sensor for gases and liquids at low concentrations. The porous fiber is treated with a reversible pH indicator dye. Initially tested for detection of ammonia vapors. 0.5 µg/l conc. easily detected.	
pH/Colormetric	Reichert, J.; Czolk, R.; Sellien, W.; Ache, H.J. – Kernforschungszentrum Karlsruhe, Institut fur Radiochemie, Karlsruhe, Germany	Chemical Sensors in Environmental Analysis: Ammonium and Cadmium Sensors	chemical sensors, ammonium, cadmium, bromophenol blue	NATO ASI Series, Series G, Ecological Sciences, Vol. 23	fiber optic	45		Addresses tasks faced in environmental analysis regarding detection of ammonium and cadmium sensors. Description and testing of fiber optic pH/colormetric fiber optic sensors. Bromophenol blue indicator dye.	
pH/Colormetric	Blyler, LL Jr.; Lieberman, RA; Cohen, LG; Ferrara, JA; Macchesney, JB – AT&T Bell Laboratories, Murray Hill, NJ	Optical Fiber Chemical Sensors Utilizing Dye-Doped Silicon Polymer Claddings	optical fiber, dye-doped, silicone polymer, ammonia, oxygen, oxazine 750 perchlorate	Polymer Engineering and Science, Mid-September 1989, Vol. 29, No. 17	plastic clad silica optical fiber	46		Dimethyl siloxane polymers applied to fused silica fibers to produce PCS optical fibers. Evanescent light propagating into fibers interacts w/ doped cladding. Oxazine 750 perchlorate dye used.	
pH/Colormetric	Muto, S., Ando, A., Ochiai, T., Ito, H., Sawada, H., Tanaka, A / Yamanashi University	Simple Gas Sensor Using Dye-Doped Plastic Fibers	organic dye, plastic fiber, sensor, tymolblue (TB) dye, optical absorption	Jap. J. of App. Phys. Vol. 28, No. 1, Jan, 1989, pp. 125-127	fiber optic absorbance measurement via pH/colormetric dye	47		Plastic optical fiber doped with polyvinylalcohol (PVA) containing tymolblue (TB) dye was used to detect alkalescent NH_3 gas.	
pH/Colormetric	Zhou, Quan; Kritz, David; Bonnell, Laura; Sigel, George H. Jr. – Rutgers U., Fiber Optics Materials Research Program, Piscataway, NJ	Porous plastic optical fiber sensor for ammonia measurement.	fiber, porous, plastic, optical, Bromocresol Purple, ammonia	Applied Optics, vol. 28, no. 11; 1 June 1989	inline optical absorption	48		Porous plastic fiber for chemical gas sensing. Based on inline optical absorption. Exibits high gas permeability and high liquid impermeability. Particularly suitable for gas conc. measurements in aqueous samples. Lower sens. limit approx. 10 ppm (?).	
pH/Colormetric	Arnold, Mark A; Ostler, Tiffany J. – Dept. of Chem., U. of Iowa	Fiber Optic Ammonia Gas Sensing Probe	fiber optic, ammonia, gas sensing, pH	Analytical Chemistry, 1986, Vol. 58, pp 1137-1140	fiber optic	49		Fiber optic ammonia gas sensing probe - pH indicator dye p-nitrophenol used to detect pH changes of internal electrolyte solution. pH change measured as light absorbance. Lower limit of detection of 5µM.	

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Sensing Technique	Author/ Organization	Title	Keywords	Citation	Sensor Type	Ref #	Other	Abstract	Comments
pH/Colormetric	Reichert, J.; Sellien, W; Ache, HJ – Institut fur Radiochemie, Kernforschungszentrum Karlsruhe GmbH, Karlsruhe, Germany	A fiber-optic sensor for the detection of ammonium in environmental waters	fiber-optic sensor, ammonium, Bromophenol Blue, waters	Fresenius J. Anal. Chem. (1990), Vol.337, page 74	optrode	50	condensation of previously entered article from another journal?	Optrode developed for determination of ammonium in aqueous solutions. Detection limit of 10 µmol/l ammonium = 160 µmol/l ammonia - responese time is 10 and 30 minutes respectively. Sensor made by dipcoating glass rod w/ thin coating of caoutchouc & BPB	
pH/Colormetric	Tabacco, Marybeth; Zhou, Quan; Nelson, Bruce – GEO-CENTERS, Inc., Newton Centre, Mass.	Chemical Sensors for Environmental Monitoring	ammonia, aromatic HC's, gases, liquds, environmental monitoring, chemical sensors	SPIE, Vol. 1587 Chemical, Biochemical, and Environmental Fiber Sensors III (1991), pp 271-277	optrodes	51		FO chem. sensors developed for monitoring of liquids and gases, utilizing porous polymer or glass optical fibers w/ immobilized chemical reagents. PPB levels of detection for aromatic HC's, hydrazine, ethylene. Sensors demonstrated for CO, NH3, humidity	
pH/Colormetric	Solorzano, Lucia – Institute of Marine Resources, U. of Cal. San Diego	Determination of Ammonia in Natural Waters by the Phenolhypochlorite Method	ammonia, waters, phenolhypochlorite, indophenol blue	Limnol. Oceanogr., Vol. 14, 1969.	chemical indicator reactions	52		Using indophenol blue dye to determine ammonia in aqueous solutions. Reaction at high pH of ammonia, phenol, and hypochlorite. Eliminates interference due to precipitation by complexing magnesium and calcium with citrate.	
pH/Colormetric	Golubkov, S.P.; Vasilenko, N.A.; Potyrailo, R.A.; Kovtun, V.S.; Borsuk, P.S. – Analytical Instruments Research Department of Special Instruments Research Institute, Kiev Polytechnic Institute, Kiev, Ukraine	Application of pH Dyes for Ammonia Sensing by Portable Analyzer	pH dyes, ammonia, portable analyzer	SPIE, Vol. 1637 Environmental and Process Monitoring Technologies, 1992, pp. 227-232	dye-film coated glass	53		Portable device, continuously measures ammonia gas concentrations. Detection is based upon reversible changes in optical transmittance of a dye-film coated on glass support.	
pH/Colormetric	Dickert, F., Schreiner, S., Mages, G., Kimmel, H /Erlangen University, Central R&D	Fiber-Optic Dipping Sensor for Organic Solvents in Wastewater	Triphenylmethane dyes, organic solvents, optical absorbance	Anal, Chem. 1989, 61, 2306-2309	fiber optic absorbance measurement	54		Gas-permeable membrane separated the sensor layers from the aqueous solution. A sensing layer of triphenylmethane was coated on the end of a fiber optic cable. Detection was base on absorbance.	

Table B.1. Reference Matrix

Sensing Technique	Author/ Organization	Title	Keywords	Citation	Sensor Type	Ref #	Other	Abstract	Comments
pH/Colormetric	Shahriari, Mahmoud R.; Sigel, George H. Jr.; Zhou, Quan – Rutgers U., Fiber Optics Mat. Research. Program, Piscataway, NJ	Porous glass fibers for high sensitivity chemical and biological sensors.	glass fibers, chemical, biomdedical, sensors, gases, liquids, low concentrations, bromocresol purple	SPIE, vol. 838, Fiber Optic and Laser Sensors V (1987)	fiber optic	55		Porous optical fiber developed for use as sensor for gases and liquids at low concentrations. Porosity gives high surface area to fiber. Bromocresol purple dye. Initially tested for detection of ammonia vapors. 0.5 µg/l conc. easily detected.	
pH/Colormetric	Klein, R.; Voges, E. – U. Dortmund, Lehrstuhl fur Hochfrequenzteknik, Dortmun, Germany	Integrated-optic ammonia sensor	ammonia, integrated-optic, indicator dye, evanescent-field absorption	Sensors and Actuators, B, vol 11 (1993), pp 221-225	integrated optic/evanescent field absorption	56		Integrated-optic ammonia sensor, evanescent-field absorption, using strip waveguide, coated w/ immobilized indicator dye. Short response time & long lifetime. Capable of detecting ammonia in ppb range.	
Absorption	Giuliani, JF; Wohltjen, H; Jarvis, NL – Surface Chem. Branch, Chem. Div., Naval Research Lab, Wash. DC	General Theory and Design Considerations for Optical Waveguide Chemical Vapor Sensors	waveguide, optical, chemical vapor, theory, design	Report from DTIC (Defense Technical Information Center), AD-A148 505	Waveguide ATR spectroscopy	57		Guided waveguide device using chemical selective coating showed reversible response to ammonia vapors. 40% relative humidity produces a detector response which completely obscures the ammonia vapor signal below 1000 ppm.	Anhydrous ammonia detection only. Serious water vapor interference
Absorption	Ataman, O. Yavuz;Mark Jr., Harry B. – Dept. of Chem., U. of Cincinnati, Cincinnati, OH	Determination of Ammonia in Aqueous Solutions by Infrared Spectrometry Following Preconcentration on Zeolite	ammonia, aqueous solutions, R spectrometry, zeolite	Analytical Chemistry, Vol. 49, No. 9, August 1977, pp. 1331-1335	zeolite matrix	58		NH4+ preconcentrated on zeolite matrix - zeolite pellet's R spectrum is taken - intensity of bending vibration band is used to calculate the NH3-N concentration in the sample solution. Results of analyses: 5-12% mead deviation between 14.0 to 0.50 ppm	Ammonium detection. Not in situ or real time
Absorption	Sanghera, J. S., Kung, F. H., Pureza, P. C., Nguygen, V. Q., Miklos, R. E., and Aggarwal, I. D/ NRL, University of Maryland, Virginia Polytechnic Institute, and SFA Inc.	Infrared Evanescent-Absorption Spectroscopy with Chalcogenide Glass Fibers	telluride fiber-optic, evanscent spectroscopy	Applied Optics, Vol. 33, No. 27, pp. 6315-6322, 1994	evanscent fiber optic/absorption	59		Telluride glass fibers were used to detect compounds in aqueous solutions using evanescent-absorption spectroscopy. Detection limits of ethanol in water were less than 2 vol. %.	Info on fiber optic R spectroscopy. No data on ammonium detection.
Absorption	Katzir, A.; Simhony, S. – School of Phys. and Atronomy, Raymond and Beverly Sackler Faculty of Exeact Sciences, Tel-Aviv U., Tel-Aviv, Israel	Remote monitoring of ammonia using a CO2 laser and infrared fibers	ammonia, laser, infrared fibers, monitoring	Applied Physics Letters, Vol. 47(12), 15 Dec. 1985, pp. 1241-1243	silver halide fibers w/ absorption cell	60		Silver halide fibers used for transmitting R radiation from CO2 laser to absorption cell. Absorption of CO2 laser lines in ammonia gas was measured in remote cell. First time demonstration of use of R fibers for spectroscopy in mid and far IR.	NH3 detection only

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Sensing Technique	Author/ Organization	Title	Keywords	Citation	Sensor Type	Ref #	Other	Abstract	Comments
Absorption	Meienburg, W; Neckel, H; Wolfrum, J – Pysikalish-Chemisches Inst. der Universitat, Im Neuenheimer Feld 253, Heidelberg D-6900, Germany	In Situ Measurement of Ammonia with a 13CO2-Waveguide Laser System.	in situ, ammonia, waveguide, laser	Applied Physics B, vol. 51, pp 94-98, 1990	turnable CO2 waveguide laser	61		Sensor measures absorption w / tunable CO2 waveguide laser frequency modulated between two adjacent emission lines. Autocalibrated. High spec. resolut. suppresses interference from other species. Detection limit of 1 ppm reached @ time constant of 5 sec	NH3 detection only
Absorption	Feher, Miklos., Martin, Philp., Rohrbacker, Andreas., Soliva, Anton., Maier, John /University of Basel	Inexpensive near-infrared diode-laser-based detection system for ammonia	diode-laser, absorption, gas sensor	Applied Optics, Vol. 32, No. 12 20 April 1993	diode laser absorption spectroscopy	62		Near-infrared diode-laser with a 1 meter absorption path in used to detect NH3 with a sensitivity of 2 ppm	NH3 detection only

Table B.2. Specification Matrix

Sensing Technique	Ref #	Sensitivity	Response	Dynamic Range	Response Time	Selectivity	Accuracy	Reversible	Stability	Comments	Meets Requirements
Acoustic Wave	7	6.5 ng/liter	linear	1-2 orders	unknown	dependent on relative humidity and temperature	unknown	yes	unknown	Using denuder tube for sampling gaseous ammonia; detection with piezo quartz crystal. Tube coated w/ tungsten oxide; crystal w/ pyridoxine hydrochloride. 29 ng/l of ammonia in air detected w/ signal to background ratio of 14:1 w/ enrichment ratio of 900	no: gas sensor
Refractive Index	12	percent level	nonlinear	30 to 70% concentration	real time	unknown	+/- 0.3%	yes	< 0.2% short-term and < 0.5% long-term	Fiber optic sensor inserted into refrigerant absorption fluid at user-definable points to make real time measurements of fluid's refractive index. Thermocouple also used. Temperature and concentration measurements enable in-line monitoring and control.	This work was done for lithium-bromide solutions. Applicable to other binary mixtures have refractive indexes within 1.4-1.5 range.
Refractive Index	13	percent level	nonlinear	30 to 70% concentration	real time	unknown	+/- 0.3%	yes	< 0.2% short-term and < 0.5% long-term	Fiber optic sensor inserted into refrigerant absorption fluid at user-definable points to make real time measurements of fluid's refractive index. Thermocouple also used. Temperature and concentration measurements enable in-line monitoring and control.	This work was done for lithium-bromide solutions. Applicable to other binary mixtures have refractive indexes within 1.4-1.5 range.
Electrode	15	0.7 µM	linear	two orders	< 1 min	Responsive to cation of K, NH4+, Rb, and Cs	very good	unknown	very good (standard deviation below 5% over period of several hours)	Electrode coated with hexacyanoferratic films to detect nonelectroactive cations in a flow-injection system. This electrode responded to NH4+ ions with detection limits of 0.2µM and 2 orders of linear response.	possible: ammonium-ion electrode
Electrode	16	0.1 mg/l	nonlinear	2 orders	function of concentration (typically 15 min)	Salinity response	unknown	yes	stable for a period of days	Ammonia measurements were automated using a computer and an Orion Ammonia Electrode Model 95 10.	NH3 sensor only
Electrode	17	1.0 mg/l	nonlinear	2 orders	function of concentration (typically 15 min)	Salinity response	unknown	yes	stable for a period of days	An Orion Ammonia Electrode Model 95-10 was used to determine levels of ammonia in sea water between 0.1 and 2.0 mg/l	NH3 sensor only
Electrode	18	0.02 mg/l	nonlinear	3 orders	30 sec to 5 min	Salinity response	unknown	yes	stable for a period of days	An Orion Ammonia Electrode Model 95-10 was investigated by the EPA.	NH3 sensor only
Electrode	19	0.02 mg/l	nonlinear	3 orders	30 sec to 5 min	Salinity response	unknown	yes	stable for a period of days	An Orion Ammonia Electrode Model 95-10 was used to determine levels of ammonia in sea water and waste . Its' performance was compared to those from the indophenol blue method.	NH3 sensor only
Electrode	20	0.1 mg/l	nonlinear	4 orders	function of concentration (typically 15 min)	Salinity response	5-10%	yes	stable for a period of days	An Orion Ammonia Electrode Model 95-10 was used to determine levels of ammonia in sea water . Analysis below 10 ppb had longer equilibration time.	NH3 sensor only
Electrode	21	0.2 µM	nonlinear	unknown	function of concentration (typically 15 min)	membrane dependent	+/- 0.1 µM	yes	stable for a period of days	The electrode senses change in pH of an internal NH4OH-chloride solution. The electrode is a commercially available Orion Research model 95-10. Requires 150 ml sample size.	NH3 sensor only
Electrode	23	2 µM	linear	3 orders	< 60 sec	membrane, dependent	+/- 10%	yes	unknown	Amperometric ammonium-ion selective PVL-nitrobenzene gel elcetrode containing dibenza-18-crown-6 was covered w/ gas permeable membrane. Sensor gave current response proportional to the ammonia concentration from 2 to 200 micromol/cubic dm.	possible: ammonium-ion electrode
Thermal	24	few ppm	nonlinear	4 orders	2 sec for peak /30 to return to baseline, depending on thermal capacity of sensor and environment	membrane dependent	unknown	no: acid-base reaction	unknown	Two different acid membranes used on pyroelectric sensor: nonanoic and ethanesulfonic acid. Signals result from heat due to NH3-acid membrane interaction.	unlikely: senses exothermic reaction which may be hard to interpret in the heat pump cycle
Electrical Conductivity	30	unknown	unknown	unknown	unknown	unknown	unknown	unknown	unknown	TSM acoustic wave sensors coated with polymerizd pyrrole by electrochem. methods. Films characterized w/ scanning electron microscope. Freq. decreases for sensors exposed to methanol, toluene, and ammonia evaluated.	

Table B.2. Specification Matrix

Sensing Technique	Ref #	Sensitivity	Response	Dynamic Range	Response Time	Selectivity	Accuracy	Reversible	Stability	Comments	Meets Requirements
Electrical Conductivity	31	1.5 - 5.4 ppm	linear		15 min ?	dependent on photoconductivity changes	probably good	unknown	unknown	Determination of NH3 in flowing N2 or air demonstrated by monitoring changes in photoconductivity of chloroindium phthalocyanine (InPc-Cl) and chlorogallium phthalocyanine thin films deposited of platinum silicide microcircuits. Response: 1.5 to 5.4 ppm	
Electrical Conductivity	32	<0.5 ppm	exponential		dependent upon thickness of film	good			pretty good	Vapor-sensing method developed is compatible w/ monolithic silicon microelectronics tech. Elec. conduct. changes caused by vapor interact. w/ very thin films of organic semiconductors are shown to be sensitive, reproducible, rapid, and stable detectors.	
pH/Colormetric	43	60 ppm	linear	3 orders	dependent of concentration: 1000 ppm = 3 min	dependent on relative humidity	+/- 1%	yes	unknown	Small glass capillary tube fitted with LED and photoresistor detector to form multiple reflecting optical waveguide device. Capillary coated w/ oxazine pherchlorate dye demonstrated capability of reversible sensing of ammonia vapors. 60 to 1000 ppm	possible: the dye film rapidly changes color from blue to red in the presence of ammonium hydroxidel
pH/Colormetric	47	10 ppm	(Io-I)/Io	3-4 orders	dependent of concentration: 1000 ppm = 12 min	responds to acid gases, very dependent of relative humidity	~5%	yes	unknown	Plastic optical fiber doped with polyvinylalcohal (PVA) containing tymolblue (TB) dye was used to detect alkalescent NH3 gas.	unlikely: alkalenscent gas-phase sensing, relative humidity dependent
pH/Colormetric	54	15 ppm	excellent linearity		10 seconds	dependent on colormetric response of dye	dependent on temperature of sensor head		depends on constant vapor pressure at sensor head. This depends on temperature	Gas-permeable membrane separated the sensor layers from the aqueous solution. A sensing layer of triphenylmethane was coated on the end of a fiber optic cable. Detection was base on absorbance.	
Absorption	57	60 ppm @ 40% RH	linear	3 orders	dependent of concentration: 6000 ppm = 5 min	Anhydrous ammonia detection only. Serious water vapor interference	unknown	yes	unknown	Guided waveguide device using chemical selective coating showed reversible response to ammonia vapors. 40% relative humidity produces a detector response which completely obscures the ammonia vapor signal below 1000 ppm.	Anhydrous ammonia detection only. Serious water vapor interference
Absorption	58	0.5 ppm	unknown	1 to 2 orders	long	very selective	5-12%	no	unknown	NH4+ preconcentrated on zeolite matrix - zeolite pellet's R spectrum is taken - intensity of bending vibration band is used to calculate the NH3-N concentration in the sample solution. Results of analyses: 5-12% mead deviation between 14.0 to 0.50 ppm	Not in situ and not real time response
Absorption	60	35 ppm with 19.5 cm path length	logarthmic	large	immediate	very selective	high	yes	unknown	Silver halide fibers used for transmitting R radiation from CO2 laser to absorption cell. Absorption of CO2 laser lines in ammonia gas was measured in remote cell. First time demonstration of use of R fibers for spectroscopy in mid and far IR.	unlikely: gas-phase sensing only
Absorption	61	1 ppm	logarthmic	large	5 sec	very selective	5%	yes	unknown	Sensor measures absorption w/ tunable CO2 waveguide laser frequency modulated between two adjacent emission lines. Autocalibrated. High spec. resolut. suppresses interference from other species. Detection limit of 1 ppm reached @ time constant of 5 sec	unlikely: gas-phase sensing only
Absorption	62	2 ppm	logarthmic	probably large (4 5 orders)	1 second	possible absorption overlaps with other compounds	probably good	yes	limited on small oscillations in the line locking of the diode laser	Near-infrared diode-laser with a 1 meter absorption path in used to detect NH3 with a sensitivity of 2 ppm	questionable: sensing depends on constant vapor pressure at sensor head. This depends on temperature

Appendix C

Commercial Ammonia/Ammonium Measurement Technologies

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Commercial Ammonia/Ammonium Measurement Technologies

Introduction

The information summarized in the main body of this report was compiled from advertising specifications and from telephone contacts in October 1994 with fifty commercial sources. In these conversations, as much specific information as possible was gleaned from applications engineers regarding technologies that would be most appropriate for continuous on-line localized determinations of ammonium hydroxide in the concentration range between 1% and 60%. Other application constraints included pH between 10 and 12, an operating pressure between 15 and 80 psig, operating temperature between 40°F and 200°F, and the presence in the flow of a small amount of sodium hydroxide.

Detection/Analysis Technologies

Nine methods for detecting ammonia/ammonium concentration were identified in this investigation:

1. Spectrometry/Photometry
2. Wet Chemistry Colorimetric Detection
3. Wet Chemistry Ion Selective Detection
4. Ion Selective Probes
5. Fiber Optic Probes
6. Ionized Mobility Spectrometry
7. Electrodeless Conductivity
8. Straight Acid/Base Titration
9. Glass Sample Tube or Ampule.

Each of these methods is described in the following paragraphs.

1. Spectrometry/Photometry

Near-infrared (IR) photometry can be used for assessing high concentrations of ammonium hydroxide. This technology may be better for concentration detection at higher concentration levels than it is for detection at lower concentration levels (under 1%). This approach is noninvasive and does not contaminate the flow. However, a small portion of the flow must normally be directed through an optical test cell in the instrument. Dual-beam, comparative-filter photometry measures the absorbance at specific wavelengths by employing narrow bandpass optical filters. One line is selected for its unique spectral identification with the test substance, and the reference line is selected in an area of the spectrum where there is very little absorbance. Potentially good test lines for ammonium hydroxide exist at 2.2 microns and 1.21 microns. Another possibility is to monitor the water absorption line (2.6 microns). The best lines for ammonia vapor are in the 10.2- to 10.4-micron region. The vendor could provide a custom-designed slipstream sampling system to interface with our system. Alternatively, it may be possible to custom-integrate a comparable optical test cell into our loop that could interface with the instrument through fiber optics. Such an interface might provide the most localized measurements and fastest response time. (Custom Sensors already has developed such a fiber-optic-coupled probe that interfaces with the HP942.) A photometer can handle up to 150°C and up to 500 psig. It provides a continuous on-line process output signal. The delay between input and output is roughly equal to the time that it takes to fill the cell volume four or five times. Therefore, the faster the test flow can be pumped through the cell volume, without exceeding 500 psig, the more responsive the measurement will be. Accuracy of the dual-beam comparative method is approximately 1%. Another spectrometry/photometry approach uses an acoustically tuned crystal to assemble a unique signature by scanning a set of wavelengths. This approach has an accuracy closer to 0.01%. These IR approaches may be aggravated by the background natural heat energy present at higher temperatures. However, IR techniques are the least susceptible to being affected by the presence of sodium hydroxide in the test solution. The dual-beam comparative line photometer costs range from $15K to $20K; the spectrum-scanning type of photometers cost about $45K. Similar instruments operating in the ultraviolet (UV) range have potential application for assessing concentrations of lithium bromide. This type of instrument is available from Custom Sensors & Technology, Foxboro, or ABB.

2. Wet Chemistry Colorimetric Detection

In the wet chemistry colorimetric approach, the sample is mixed with a predetermined amount of a reference reagent, and the color change is detected with a photometer or interference filter. This technology is also sometimes called a segmented flow instrument or flow injection instrument. These measurements can be automated for continuous on-line applications, but it is technically a batch process with a delay of from 30 s to 5 min from input to output. Typical numbers are 80 samples per hour, with a 4-min delay on each determination. The process is slightly faster than the wet chemistry ion-selective approach because once the color change has started, it is possible to predict the outcome from the initial curve. The colorimetric analysis approach is also more exact than the ion-selective electrode alternative, and it is affected less by temperature changes. However, the wet chemistry ion-selective technology can be used to monitor much higher concentrations of ammonium hydroxide. In the colorimetric approach, operating pressure problems are alleviated because a peristaltic pump in the process works at the same pressure at which the system is looking. This approach is used primarily for gas or vapor testing, but it has been adapted for the assessment of ammonium hydroxide concentrations by Scientific Instruments (0 to 200 ppm) and by Perstorp (0 to 10,000 ppm, strictly batch mode). These instruments cost from $15k to $50K. This type of instrument is available from Applikon, Lachat, Orbeco, Perstorp, Bran & Luebbe, and Scientific Instruments.

3. Wet Chemistry Ion-Selective Detection

The wet chemistry ion-selective approach has the potential to assess concentrations of ammonium hydroxide as high as 20% to 50%. In this approach, the sample is mixed with a predetermined amount of a reference reagent, and the change in conductivity is detected with an ion-selective electrode. This measurement can be automated for continuous on-line applications, but it is technically a batch process with a delay of from 1 to 5 min from input to output. This approach is used for both vapor and liquid testing. Standard concentration ranges include 0 to 10 ppm to 0.1 to 10,000 ppm. Polymetron offers dilution options of 20:1 and 50:1 that could expand this range up to 20% or 50%. They cost from

$15k to $30K. This type of instrument is also available from Calibrated Instruments (Bochum), Applikon, Astro/Polymetron, Bran & Luebbe, and Capital Controls.

4. Ion-Selective Probes

This approach uses an inexpensive ($300) ion-selective electrode probe and a standard pH meter (about $1500). A fixed reagent amount is added to an off-line sample; after a stabilization period of about 5 min, the meter reading is recorded. The ion strength adjuster is specific to the substance being quantified. For ammonia, it is sodium hydroxide. For ammonium, it is sodium chloride. For bromide, it is sodium nitrate. This type of determination is not affected by a small amount of sodium hydroxide already in solution. The only interfering chemicals are volatile amines. At a pH of 11 or 12, the ammonia ions in a test solution dissociate. This can make ammonium concentration measurements harder to perform. This problem is further aggravated if there is even a trace presence of an acid in the solution. Maximum concentration ranges are for ammonia = 17,000 ppm, for ammonium = 18,000 ppm, and for bromide = 79,000 ppm. The operating temperature range for ammonia and ammonium is 0°C to 60°C and for bromide is 0°C to 80°C. Ion-selective electrode monitors are available from Brinkman (Metron) and HNU. HNU claims that they do not add any chemicals and that their probe can be placed directly in the flow to take continuous on-line measurements.

5. Fiber Optic Probes

This approach employs an in situ fiber optic probe. It has been used to assess concentrations of ammonium hydroxide in the 10% range (Research International). The technique is free from chemical contamination problems and provides a highly localized measurement but placement may physically disrupt the flow. The diameters of probes from several different vendors range from .014 in. to .39 in.. This technology is very new and highly competitive. Several products are new on the market or in the final stages of being released. They employ various methods such as impregnating ionic reactive chemicals or litmus substances in the glass of the fiber or by coupling the optical fiber to some kind of semiconductor element. There is some concern that the glass fibers may not hold up well under the corrosive environment associated with a pH of 12. They all provide a continuous on-line process signal. Most are best suited to concentration determinations of vapor and liquids in the ppm levels. Measurements made with such probes are not likely to be affected by the presence of sodium hydroxide. These probes may not perform well at higher temperatures. Costs range from $2.5K to $6K. Products are either announced or available from Custom Sensors & Technologies, Lightsense, Research International or Geo-Centers.

6. Ionized Mobility Spectrometry

The ionized mobility spectrometry approach is used for the continuous monitoring of inorganic acid compounds. It can be used for very low concentration determinations of both ammonia and bromide in the vapor state. Typical concentration ranges are 0 to 5 ppm and 0 to 20 ppm. It uses Ni 63 as the radiation source. It is an atmospheric pressure based time-of-flight analytical technique similar to mass spectrometry. It has an operating temperature range of from -40°F to 122°F. This product is available from Environmental Technologies Group and PCP.

7. Electrodeless Conductivity

This approach assesses ammonium concentration by making a simple conductivity determination. It can handle concentration levels up to 60%. It provides a continuous on-line process signal. Such an instrument requires no chemical additive. It is available in either the flow-through test cell (off-line) or dual probe (in-the-flow on-line) configuration (Polymetron). It has a 0.1% accuracy and can handle concentrations approaching 100% (Polymetron). However, because the calibration of the instrument is based on the two slopes associated with the two sides of a parabolic curve the measurement range between 25% and 30% is not usable. This instrument has an operating temperature range up to 300°F and it is less susceptible to pH changes than the ion-selective approach. However, if it is true that ionic dissociation aggravates conductivity determinations at pH levels around 12 then this method may be less promising. For our application two such probes would have to be put directly in the flow to make localized measurements. The probes are about 3 in. long and about 5/8 in. in diameter. The product offered by Foxboro has an operating temperature up to 200°F and an accuracy of from 2%-4%. Electrodeless conductivity instruments are available from Foxboro or Polymicron for between $1800 and $3K.

8. Straight Acid/Base Titration

The titration approach can be used to assess ammonium hydroxide concentrations as high as 60%. Units are available to perform this operation either manually or automatically. The on-line automated instrument takes a sample and titrates it with a standard solution of hydrochloric acid. When the pH detector indicates that the solution is neutral the ammonia concentration is calculated based on how much of the standard HCl solution was consumed. The delay from input to output is typically about 5 min. An automated titration analyzer costs from $15k to $30k. These instruments are available from Brinkman (manual), Orbeco, Perstorp (automated) and Applikon (automated).

9. Glass Sample Tube or Ampule

This approach involves the use of manually activated sampling tubes or ampules. These are used for gas and vapor concentration assessment for ammonia. The tube type of system requires the use of a $400 sampling pump to acquire the sample. The self-contained tube contains phosphorus oxide that is neutralized by the ammonia vapor producing a visible stain that is directly read against a calibrated concentration scale. The ampule type of system takes the sample automatically but requires a $500 reader to produce the resulting determination. Concentration ranges include from 0 to 1.5 ppm to 10 to 1000 ppm. Sampling units cost from $1 to $8 each. Sampling tube products are available from Sensidyne and Chemetrics.

Conclusions

Only four of these approaches offer much potential for the on-line assessment of ammonium hydroxide concentrations between 20% and above. These are photometry, titration, electrodeless conductivity and wet chemistry ion-selective. Most of these approaches are available as automated on-line processing instruments for between $15k and $30k. The least expensive technique is electrodeless conductivity at between $2K to $3K.

Dual beam comparative photometry may be the best choice. It can handle concentrations up to 60% and costs between $15k and $25k. This approach provides 1% accuracy, it is physically and chemically noninvasive and it is insensitive to the presence of sodium hydroxide in the flow. It is insensitive to operating pressure, however, there may be some background noise due to the IR at higher temperatures. It is possible that a customized fiber optic test cell could be designed to meet our needs. The development of such a configuration would make possible localized measurements and increased processing speed. That would not be possible using the slipstream sampling method normally associated with this technology.

The second possible approach is to use an automated titration analyzer. The concentration range of this technology can extend up to 60% and it costs between $15k and $30k. This approach requires that a sample be taken and that its chemistry be altered while assessing its concentration. The delay from input to output is typically 5 min.

The third potentially useful technology is the electrodeless conductivity approach. This method can assess concentrations well above 60% with an accuracy of 0.1% and costs between $2k to $3K. It is not chemically invasive but for localized on-line measurements two probes would have to be placed in the flow, which could be physically invasive.

The fourth possible approach is the wet chemistry ion-selective approach. The concentration range of this technology normally is up to 1%, but it can be extended through dilution up to 20% and even 50% (Polymetron). This is not the ideal approach because it is primarily a batch process. It requires that a sample be drawn and the chemistry of the sample be changed before the test is performed. The delay from input to output is typically 2 min (up to 5 min). (Note the wet chemistry colorimetric approach is slightly faster, is more accurate and is less susceptible to temperature changes but it has an upper concentration limit of only 10%.)

Vendors of Ammonia Sensors

Aldrich Chemical Company
1001 W. St. Paul Ave.
Milwaukee, WI 53233
800-558-9160

Aldrich carries sensidyne tubes that connect to a handheld piston type of sampling pump. These direct reading tubes provide a stain with a length proportional to ammonia concentration (in ppm). Sensidyne tubes are also available that do not require a pump. The first type requires a $400 pump. The disposable tubes are available in ranges of 1 to 60 ppm, 1 to 200 ppm, and 10 to 1000 ppm; their cost is $40 for a pack of 10. Sensidyne tubes that do not require a pump are available in the range of 25 to 500 ppm and cost $50 for 10.

Alltech Associates
2051 Waukegan Road
Deerfield, IL 60015
708-948-8600

Alltech sells an inorganic ammonia analyzer for determining very low ammonia concentrations in soils, drinking water and waste water. This type of product can also detect nitrates and nitrites. It uses a pump and sample system with processing based on conductivity. The range of measurement is 100 ppb to 1000 ppm. Alltech does not offer any high-concentration or on-line monitoring instrument.

Brinkman Instruments, Inc.
One Cantiauge Road
Westbury, NY 11590-0207
516-334-7500
800-645-3050 FAX
206-881-0634, Jerry Boggan or voice mail 800-274-6562 ext. 442

Their ion-specific electrodes operate in many ranges from a couple parts per million up to 120 ppm. To stay in calibration over this range, three separate standards are needed. To stay in calibration over the extended range of 100 to 1000 ppm, additional standards are needed. The lab version of the ion-selective sensor based instrument that they sell is limited to processing a sample that has been removed from the test stream. However, it can handle concentrations up to 60%. Measurements should not be affected by the presence of sodium hydroxide. Concentration conversions: 1 mg per *l* is 1 ppm, to calculate concentration for ammonium hydroxide the molecular weight of ammonia and water has to be taken in consideration The other term that is commonly used for higher concentrations is gram percent. Their instrument will measure 60% solutions directly with no predilution but for very high concentrations they have to go to manual titration methods. Their lab unit is made by Metrohn sold by Brinkman. An ion-selective unit that can be used in on-line applications is make by Metrohn and sold by Applikon of Holland. This sensor can be put directly in the test stream.

Applikon
Brion Dalton
516-431-7985

The Applikon unit uses an ion-selective sensor based technology and is designed for on-line in situ applications. This instrument is limited to determining ammonia concentrations in only the ppm levels and even then only for ammonia vapor, not ammonium hydroxide. This ion-selective analyzer is only useful for ammonia waste water (ppm levels). It uses on line ion-selective electrodes. An ion strength adjustment buffer is added to the sample to release gas because they are using a gas membrane ion-selective electrode. This process also takes 5 min from input to output. Brion Dalton says that their titration/photometric analyzer is capable of measuring concentrations as high as 60%. It is designed for automated on-line operation in a batch mode and their is typically a 5 min delay from the time that the sample is acquired to the time when a quantitative result is available. The typical configuration is a rack mount batch operated robotic workstation. The measurements are not continuous. A sample is taken between 0.5 cc and 0.1 cc in size and hydrochloric acid standard solution is added until a color change is registered. The concentration calculation is made based on how much HCl was used. The cost of a low-end single stream analyzer using this technology is about $15K. Either the ion-selective or the titration/photometric unit requires a source operating at less than 29 psig and less than 90°C. These pressure and temperature limits seem dictated by the solenoid valve that they use rather than the chemistry of the process.

Calibrated Instruments, Inc.
200 Saw Mill River Road
Hawthorne, NY 10532
914-741-5700
914-741-5711 FAX

They sell a series of ammonia analyzers that cost $30K and up. The sample is mixed with a regent with known conductivity and the resulting change in conductivity is monitored. The process is known as a wet gas test. This unit is a continuous analyzing and monitoring instrument that samples the flow at a given point. Ranges extend from 0-10 ppm up to 0-400 ppm. The package is generally rack mount but it can be put in a portable package of about 30-35 lbs. It can be used either portable or be permanently installed on-line. This product is the micro gas analyzer line. They also offer a more elaborate ultra gas analyzer line. The latter are mainly for lab use. Bochum in Germany is the actual manufacturer.

Calibrated Instruments specializes in process control and does much work with chemical processing firms such as those in the petroleum industry. To apply their micro gas analyzer to our task they would first need to get the test material into their instrument at a pressure lower than our maximum of 80 psig. Calibrated Instruments also has an instrument designed to measure ammonia content in boiler water. This is German made and evidently most technical support for the products is still in Germany. It looks like it may be direct reading and not well suited to on-line continuous monitoring.

Capital Controls Company, Inc.
PO Box 211
Colmar, PA 18915
215-997-4000 or 215-822-2901
800-523-2552 FAX
Walter Gruce

They offer the series A100 Aztec microprocessor ion-selective monitor for ammonia. It provides continuous on-line monitoring, data logging, and alphanumeric display of ammonia concentration in mg/*l*. It is designed for measurements of liquid ammonia that are first treated with sodium hydroxide to release the ammonia vapor that is then detected with an ion-selective gas electrode. The system provides outputs to a recorder or microprocessor I/O. It is selectable to measure either ammonia or ammonium (NH_3N in mg/*l* in ranges up to 20 mg/*l*). Higher ranges are available on request.

CHEMetrics, Inc.
Route 28
Calverton, VA 22016
703-788-9026
800-356-3072 FAX

They sell a glass ampule based sample and process technology. They offer different kinds of ampule readers depending on the concentration range of interest. The two types of readers are the photometric and the digital Chemet reader. These can read concentration ranges as low as 0 to 1.5 ppm and both readers are in the $500 range. She will send a catalog, they have a kit that will titrate for bromide. It is only accurate if no iodide or chloride is present.

Clean Air Engineering
500 West Wood
St. Palatine, IL 60067
708-991-3300
800-627-0033 FAX

Clean Air Engineering does not offer any products for direct monitoring of liquid ammonia. Their instruments are available for lease and are designed for monitoring air pollution.

Custom Sensors and Technology
7534 Watson Road
St. Louis, MO 63119
314-962-4555

They are very close to offering an optrode for in situ monitoring of gas phase ammonia and very low liquid concentrations of ammonia. This optrode will be based around a reversible litmus-like material immobilized in a piece of glass. It would be mounted on the end of a fiber optic probe that could be located in the process stream. They are still working on the stability and reproducibility of this product.

If the ammonia being monitored is in high enough concentration and in liquid form (very likely in our application), it is feasible to monitor concentration by watching the absorption peak for water in the IR region between 1100-2200 nm. They currently offer a product that can provide this type of measurement. This method of concentration determination works for both bromine and chlorine, but look for the absorptive peak for bromine in the UV not the IR region. Technology described in fix is associated with their fiber optic coupling to the HP 452A fixed filter based photometric analyzer or spectrophotometer with range of from 240nm to 1,000nm. They also offer a portable line of photometric analyzers that cover the range from UV to near IR. They are used to monitor chemical constituents in a flowing stream. They employ optical fibers to isolate specific wavelengths of energy from the absorbing medium.

Enmet Corporation
34680 Fairfield Court
Ann Arbor, MI 48106
313-761-1270

313-761-3220 FAX

They specialize in health and safety devices. Their ammonia gas vapor monitor is designed to monitor a stream of gaseous material such as ammonia and alarm on leak detection. The unit sounds alarm at 25 ppm. They offer portable and stationary gas analyzers in the $1000-$1200 range.

Environmental Technologies Group, Inc.
1400 Taylor Ave
Baltimore, MD 21284-9840
301-339-3146
800-635-4598 FAX
Allen Bickel

Their instruments detect both ammonia and bromide but only in gaseous state and in very low concentrations (ppm levels). Their company is the leader in the ionized mobility spectrometry approach for the detection of inorganic acid compounds. It uses Ni 63 as the radiation source. It is a time-of-flight technique similar to mass spectrometry.

Eppendorf North America, Inc.
545 Science Drive
Madison, WI 53711
608-231-1188
800-421-9988 FAX

Eppendorf does not offer this type of instrument.

Amko Systems
905 771 1444

Amko Systems does not offer this type of instrument.

FCI Fiberchem (or FCI Environmental) Inc.
1181 Grier Drive, Suite B
Las Vegas, NV 89119
702-361-7921
David LaBlanc

They only have sensors that monitor petroleum and aromatic hydrocarbons in water. This measurement is normally performed with gas chromatography, but instead they use a fiber optic chemical probe that goes directly into the test solution. The hydrocarbons attach themselves to the special chemical coating on the surface of the fiber optic cable, thereby changing the index of refraction and effecting light transmission through the fiber. The instrument is portable, has data logging capability, a 4-s response (but takes 5 min to get an analytical steady-state result), current ranges up to 20,000 ppm, potential extended range up to 100000 ppm (10%) and a price of $6200 (but will not detect ammonia).

Figaro USA Inc.

1000 Skokie Blvd
Wilmette, IL 60091
708-256-3546
708-256-3884 FAX

Their device is not a precise analytical sensor. It is used principally for alarms etc. It is a metal oxide semiconductor device, designed for gas phase only. Sensors cost about $52 each.

Foxboro
Bristol Park B521B
Foxboro, MA 02035
508-543-8750
800-521-0451 FAX
Darrel Hasslett 713-932-7777 ext. 2775

1) They offer the Miran 203 single beam IR gas analyzer It is used only for ambient air measurements. The cost is usually between $7k and $8k. It responds between 0-50 ppm. They also offer specialized units that can go as high as a 0-150 ppm range and 0-1000 ppm range. All these instruments operate at different wavelengths around10.4 or 10.36 microns. There are three basic products in the 970 series of IR analyzers. The first is the LUFT type. It is a non-dispersive IR broad band unit that operates on the principle of gross absorbance of energy. All spectral information is averaged out. The second type is the model 973 (which is the unit that he believes would best meet our needs). This unit uses a line spectral comparative technique that looks at the strength of both a reference wavelength and a measured wavelength. This is usually accomplished with filters. The third type is the LIMOR unit that puts together a signature by scanning a set of wavelengths using an acoustically tuned crystal to select the wavelengths. He would use the model 973 to look at the ammonia line at 10.2 microns rather than the water line at 2.6 microns. The cost of the model 973 line spectral comparative unit is $15k. The model 973 IR line comparison technique has an accuracy of about +/-1%.

They also have a conductivity and pH based technology that might be applied to the on-line monitoring of ammonia concentration. These would also require a flow through slipstream sampling technique. This unit is the model 873 electrode-less conductivity system. It uses no additives nor makes any changes in the chemistry of the sampled material. It would be the least exact of the 3 methods with an accuracy of between 2% and 4%. This technology is also affected by temperature but it can be compensated. They also carry direct reading electronic pH based measurement instruments that might be applied to this task.

Geo-Centers, Inc., Sensor Systems Group
7 Wells Avenue
Newton Centre, MA 02159
617-964-7070
Mary Beth Tabacco

They are in the final stages of development of a fiber optic ammonia sensor for NASA that can determine concentrations either in ammonia vapor or as ammonia dissolved in aqueous solution. Although their present application involves concentrations in the sub ppm levels, she believes that their technology might be extrapolated to higher concentrations. The advance prototype system will be evaluated by NASA for use in closed loop plant growth and for monitoring the ammonia dissolved in recirculating potable water systems and should be on the market by January 95. This sensor is designed to detect the ammonia not the ammonium. Ammonia dissolved in aqueous solution up to a pH of 12 will tend to be present in the NH3 (unionized) form. Concentration is derived by detection with a solid state element at the tip of a fiber optic probe and calculating the amount of non-ionized ammonia at any given pH from the solution of the associated acid-base equations. The sensing process that takes place at the end of the probe is closely related to the function of their pH sensor and has something to do with a combination of pH determinations. The max size of the probe tip is 1 cm diameter by 1 cm long. A PC interface board is currently available for their pH probe and a comparable interface will be offered for the ammonia sensor. The price range of the ammonia sensor is expected to be close to the $2500-$3000 cost of their pH sensor. Their process is somewhat temperature dependent and they have only tested it up to 45°C, but it might be possible to correct for use at higher temperatures. The presence of a small amount of sodium hydroxide in the solution should not affect the ammonia concentration determination unless its high enough to affect the diffusion that takes place at the sensor tip or come out of solution and build up a film on the element.

HNU Systems, Inc.
160 Charlemont Street
Newton Highlands, MA 02161
617-964-6690
800-962-6032 FAX

They offer an ion-selective electrode technology that will measure liquid ammonia concentrations. The salesperson believed that they were the type that required a filling solution but that required no additive to the sample. However, their air monitor/analyzer and gas chromatography products are the products that he is most familiar. They offer a sophisticated line of photo ionization-based instruments for process analysis. The ammonia (vapor) and ammonium/combination(liquid) probes cover a range up to 17,000 ppm and the bromide probe (now discontinued) covered a range up to 79,900 ppm. The prices for these probes range from $305 to $365 but they need to be used with a $1500 digital pH meter. The probe is suitable for continuous on-line measurements. No sampling is involved, it goes directly in the flow. The diameter of the probe is about 0.5 in..

Lachat Instruments
6645 W. Mill Road
Milwaukee, WI 53218
414-358-4200
800-247-7613 FA
Fred Brinkerhoff 303-659-3215

Their approach is wet chemistry automated dual beam colorimetry but the system. They can employ various detectors including fluorimetry, flame photometry and ion-selective electrodes. It is adaptable to on-line application, but is primarily a laboratory system. Although it is automated, this automation is limited to the batch processing of a large set of samples. The system's response for colorimetric determinations is about 30 sec and for ion-selective determinations are between 60-70 sec. The delay is shorter for the colorimetric process because it is possible to predict the solution from the initial curve instead of waiting for full color development (which takes several minutes. The ion-specific process has to go to full potential. Cost: from $20k to $50k.

Lawrence Livermore National Laboratory
PO Box 808
Livermore, CA 94550
510-422-3521
Contact: Jesse Yow

Jesse referred me to Fred Milanovich (510-422-6838) and to Bob Glass (510-423-7140) Electrochemical Sensors.

Lightsense Corporation
1513 18th Street
Santa Monica, CA 90404
714-770-3450
213-828-1045
Larry Ring

They have sensors for pH and several gases. They have performed measurements on a wide range of pH in ammonia vapor. They are not sure about application to high concentration ammonium hydroxide but the range could probably be extended. They use a fiber optic probe that incorporates fluorescent dyes that remain sealed in the probe but monitor the flow through a process of ion exchange. The real concern for them is that the dyes that they have developed are optimized for the pH range of the health appliance industry: between 6.5 to 8. A special development effort would have to be put into finding comparable dyes that would work at our higher pH levels. The device is not yet on the market. They are waiting for FDA approval. It should sell in the $6K range. Very localized continuous on-line measurements can be made with this system. The tip of the 125 micron fiber optic element is the active sensing area.

MDA Scientific, Inc.
405 Barclay Blvd.
Lincolnshire, IL 60069
708-634-2800
800-244-4632 FAX
Phil Baxter

Their ammonia gas sensing instruments cover the ranges 2.5 to 75 ppm for $5K and 2.5 to 200 ppm for $7.5K. They are designed for ambient air measurements.

Astro/Polymetron
713-332-2484 Wayne Odagard ext 29

They offer an instrument based on ion-selective electrode detection that called an on-line titrator. It is not an acid/base titration but is comparable to the other wet chemistry systems described. Although the system is designed to be automated and it can have samples pumped into it from a flowing stream, the analysis has to be a batch process. A typical processing rate is 2 min per sample. The accuracy is

0.1% and even with its built in temperature compensation the max operating temperature is 140°F. The ion-selective probe in this instrument is designed to operate within a specific pH range. Operation at a pH of 12 could cause problems. The additive chemical is added all at once and the ion-selective probe determines the amount of resulting ammonia. The normal concentration ranges are: 0.1 ppm to 10,000 ppm. They offer an automatic dilution process that may extend this range by a ratio of 20:1 or 50:1. The cost is about $12K and calibration and dilution options could bring the total up to about $16K.

They suggest using straight conductivity. Such an instrument requires no chemical additive. It is available in either the flow-through test cell (off-line) or dual probe (in-the-flow on-line) configuration. It has the same 0.1% accuracy as the method described above and can handle concentrations approaching 100%. However, because the calibration of the instrument is based on the two slopes associated with the two sides of a parabolic curve the measurement range between 25% and 30% is not usable. This instrument has an operating temperature range up to 300°F and it is less susceptible to pH changes than the ion-selective approach. However,if it is true that ionic dissociation aggravates conductivity determinations at pH levels around 12 then this method may be less promising. For our application two such probes would have to be put directly in the flow to make localized measurements. The probes are about 3 in. long and about 5/8 in. in diameter.

Nova Analytical/Biomedical
200 Prospect St.
Waltham, MA 02164
617-894-0800
617-899-0417 FAX
Barbara Peterson

They do not offer any product for monitoring ammonia, ammonia hydroxide or lithium bromide. They specialize in blood chemistry and do offer a means of analyzing the amount of lithium in blood samples.

Orbeco Analytical Systems Inc.
185 Marine Street
Farmingdale, NY 11735
516-293-4110
800-922-5242 FAX

They make the Caplan portable instrument for determining ammonia concentrations in potable water systems. The max range is 7 ppm. To operate this system, the operator adds a reagent to the sample then uses a filter to look for a color change. They also have ammonia analysis systems based on the titration process.

PCP Inc.
2155 Indian Road
W. Palm Beach, FL 33409-3287
407-683-0507
800-637-5307 FAX

Their instrument uses ion mobility spectrometry. It is designed for use in ammonia vapor concentration measurements at the ppm levels.

Research International
18706 142nd Ave NE
Woodinville, WA 98072
206-486-7831
Contact: Eric W. Sasaki, President

They do not have a specific instrument developed for ammonia concentration determination. However, they offer a very small highly sophisticated fiber-optic-based pH measurement probe that is sometimes applied to the monitoring of ammonia concentration. It is only 0.014 in. in diameter and interfaces with a PC card through a fiber optic cable. The complete package, hardware and software, costs about $6K. It has been used to monitor 10% concentrations of ammonium hydroxide. It is well-suited for on-line measurements. Their principal concern is that at a pH of 12, the glass in the electrode will deteriorate. They have worked closely with other customers to provide custom probe configurations for specialized tasks. The PC card was custom-designed, and most of the software was developed using Quick Basic and Lab View for Windows.

Rupprect and Pataschnick Company, Inc.
8 Corporate Circle
518 452 0065
Albany, NY 12203
518-452-0067 FAX

They offer no ammonia sensing product. They specialize in particulate air monitoring systems.

Scientific Instruments
200 Saw Mill River Road
Hawthorne, NY 10532
914-769-5700
800-431-1956 FAX
Burt Sherry

Their instrument is designed for the continuous on-line monitoring of ammonia hydroxide concentrations at parts-per-million levels. It uses an automated wet chemistry process that involves adding chemicals to the sample and watching for a color change using a type of interference filter. It does not process samples off-line and is designed for concentration levels up to 200 ppm. The cost is between $11K and $16K.

Sensidyne Inc.
16333 Bay Vista Drive
Clearwater, FL 34620
813-530-3602
800-451-9444 FAX

They only have a product for ambient air measurements. It is a self-contained sampling tube that contains a chemical(phosphorus oxide) that is neutralized by the ammonia and produces a visible stain that is then directly read against a concentration scale.

Sensor Solid State Services
Penn Center Plaza
Quakertown, PA 18951
215-536-1990
Contact: John Chandler, Marketing Engineer

They are strictly research and development. They do not make any standard off-the-shelf sensor.

Skalar USA Inc.
500 Oakbrook Parkway
Suite 130
Norcross, GA 30093
404-416-6717
800-782-4994 FAX
John Stephen of Precision Analytical, 206-523-9490 local representative

They carry sensors based on the wet chemistry process and ion-selective electrodes.

Technicon Industrial Systems
511 Benedict Avenue
Tarrytown, NY 10591
914-631-8000
Now Miles Diagnostics, Technicon Division
800 241 2500

They formally carried an instrument for determining ammonia levels in blood. It was originally produced by Cooper and now is completely discontinued.

National Draeger, Inc.
412-787-8383
800-922-5518

They offer the handheld Pack 2 instrument with data logging capability range for ammonia concentration is 0-300 ppm. It costs about $1100. It is designed strictly for ammonia vapor determinations. They also have the DLE kit, which uses a water sample that is drawn into a tube. It comes with two ammonia tubes for concentrations of 1.5 to 10 mg/*l* and 10 to 100 mg/*l*. The cost of the kit is $567.

Perstorp Analytical Environment
503-682-6348
800-262-3668
Ron Zabudsky 503-630-6542

Perstorp's principal instrument for ammonium hydroxide concentration measurements uses the wet chemistry colorimetric approach with an auto-analyzer. This technology is also sometimes called a segmented flow instrument or flow injection instrument. It takes a sample, adds a reagent, and uses spectroscopy to detect the resulting color change. It is capable of determining up to 1% ammonium hydroxide without dilution of the test sample. It can process up to 80 samples per hour with a delay from input to output of 4 min. This method is more exact than ion-selective electrode techniques. However, their system is designed for automated batch-mode processing and it is not well suited to on-line applications. The cost of a unit is between $15K and $20K. They market this product to the water quality industry; this technology is EPA-approved.

A second approach uses a Tecator steam distillation process on the sample followed by a straight acid/base titration, which results in a manually (direct-) read ammonia content value. This instrument costs about $5K; an automated version costs about $30K. This technology has the potential to monitor levels as high as 10%.

Perstorp owns another company that produces ion-selective probes: Ask for Ms. Davis in charge of ITM ion-selective products (800-262-3668).

Sierra Monitor Corp.
408-262-6611
Charlene Morrison

They have two principal products for sensing ammonia. The model -25 electrochemical sensor and a go/no go product that is a solid state semiconductor sensor.

Waltron Ltd.
908-534-5100
800-242-7353

They have an ion-selective probe technology (model 8232). It is designed for use in ammonium hydroxide and is microprocessor based with RS-232, RS-422 and several analog outputs at various levels. It features 2 point auto calibration, 2 alarms, and handles any 2 consecutive decades of concentration between 0.05 to 1000 ppm at any time. The cost of the unit is $10K.

YSI Inc.
513-767-7241
800-765-4974

They specialize in multi-parameter monitoring for ground water contamination. They use off-the-shelf ion-selective electrode technology to detect for ammonia and ammonium, the same type of product described elsewhere for interfacing with a standard pH meter. As mentioned elsewhere, at a pH of 11 or 12 the ammonia ions dissociate. This makes of ammonium content based on pH or conductivity harder to perform.

Bran & Luebbe, Inc.
708-520-0700

They have both lab type batch mode and on-line ammonia analyzers. The batch mode devices typically operate at 120 samples per hour and operate on the principle of adding a reagent and performing a colorimetric analysis. The on-line units use either the colorimetric additive reagent process or an ion-selective probe, depending on the desired concentrations. The range capability of the colorimetric process is 0 to 15 ppm and the range capability of the ion-selective process is 0 to 2000 ppm. They can add dilution options to these on-line monitors of either 1:5 (internal) or 1:10 (external) to extend the range up to a max of 2%. Even the on-line ion-selective unit has to pull off a sample to perform the test. The single stream unit costs about $15K. Neither dilution method affects the test flow. It is either on the stream (external) or inside the monitor (internal). The sample is buffered in the monitor to maintain a constant pH and it sits in a temperature controlled heat bath because ISE probes are sensitive to thermal changes. The unit can be set by the user to auto-calibrate periodically. Outputs include 4 to 20 mA or RS-232 or RS-422. Operational: 3% standard deviation, 3% drift, the internal thermostat is set to 40°C. The only possible chemical interference is volatile amines. It requires a sample flow rate of 2 to 10 *l*/h and a pressure of between 1.2 BAR and 10 BAR.

Cole Parmer Co.
708-647-7600
800-323-4340

Their device is based on the ion-selective technology. It consists of a $300 probe designed to be interfaced with one of their pH meters ($600 to $2000) to take manual measurements. After the reagent is added to the sample it takes 5 min to make a measurement. Instead of sensing the hydrogen ion like the pH probe, this probe senses ammonia, ammonium or bromide. The reagent added is called an ion strength adjuster (ISA). The ISA for ammonia is sodium hydroxide and the ISA for ammonium is sodium chloride. However, the presence in our flow of a small amount of sodium hydroxide would not be a problem, the only interfering materials for this technology are volatile amines. Concentrations of up to 17,000 ppm may be monitored with the ammonia electrode. Concentrations of up to 18,000 ppm may be monitored with the ammonium electrode and concentrations of up to 79,000 ppm may be monitored with the bromate probe. The operating temperature range of the ammonia/ammonium electrode is 0 to 50°C and the operating temperature range of the bromide electrode is 0 to 80°C.

Engineered Systems & Design
302-456-0446
800-648-9355

They manufacture three products, all of which are based on the ion-selective technology. They offer both handheld and benchtop models, but none is automated or designed for on-line monitoring. She suggested I try Orion or Corning, both of which also offer ammonia sensing products based on the ion-selective technology.

HF Scientific, Inc.
813-337-2116
800-798-2116
Bill Lizenby

They currently only offer a handheld test kit. They specialize in on-line process monitoring devices and they are currently seriously looking at the possibility of developing a liquid ammonia on line instrument.

Quantum Analytic
800-992-4199
George Smagernoff

They lease gas chromatography and liquid chromatography equipment and suggests that we look into LC as a possible solution to our requirement.

ABB Process Analytic
Lewisberg, West Virginia
304-647-4358 ext 206
346-7205
Kyle Jones

Their major products are a gas chromatograph and a photometer. Their application's engineer advises him that high concentrations of ammonium hydroxide can best be determined with Near IR photometry. It seems that measurements under 1% are harder to make using this technology. This approach is non invasive and does not contaminate the flow. However, a small portion of the flow must be directed through an optical test cell in the instrument. It measures the absorbance at specific wavelengths determined by narrow bandpass optical filters. One line is selected for its unique spectral identification with the test substance and the reference line is selected in an area of the spectrum where there is very little absorbance. They recommend test lines at 2.2 microns or 1.21 microns for ammonium hydroxide. They noted that instrument vendors who claim that 10.2 to 10.4 microns was a good test region were optimizing for the detection of ammonia vapor. Their dual-beam filter photometer most suitable for this application costs about $20k without the sampling option and for an additional $5K they could provide a custom-designed slipstream sampling system to meet our requirements. This photometer can handle up to 150°C and up to 500 psig. The delay between input and output is roughly equal to the time that it takes to fill the cell volume 4 or 5 times. Therefore, the faster the test flow can be pumped through the cell volume, without exceeding 500 psig, the more responsive the measurement will be. The delay is typically not more than 30 s. He believes that our lithium bromide application could best be handled by their $24K UV range instrument. However, they have never tried such a measurement.

Innovative Sensors
714-799-8781
Stephen Ruff

Innovative Sensors manufactures ion-selective electrodes that serve as the primary elements for instruments offered by many other firms.

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