

# Ammonia sensors and their applications—a review

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Received 14 May 2004; received in revised form 12 November 2004; accepted 15 November 2004

Available online 16 March 2005

## Abstract

Many scientific papers have been written concerning gas sensors for different sensor applications using several sensing principles. This review focuses on sensors and sensor systems for gaseous ammonia. Apart from its natural origin, there are many sources of ammonia, like the chemical industry or intensive life-stock. The survey that we present here treats different application areas for ammonia sensors or measurement systems and different techniques available for making selective ammonia sensing devices. When very low concentrations are to be measured, e.g. less than 2 ppb for environmental monitoring and 50 ppb for diagnostic breath analysis, solid-state ammonia sensors are not sensitive enough. In addition, they lack the required selectivity to other gasses that are often available in much higher concentrations. Optical methods that make use of lasers are often expensive and large. Indirect measurement principles have been described in literature that seems very suited as ammonia sensing devices. Such systems are suited for miniaturization and integration to make them suitable for measuring in the small gas volumes that are normally available in medical applications like diagnostic breath analysis equipment.

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**Keywords:** Gas sensors; Ammonia; Miniaturization

## 1. Introduction

Thousands of articles have been published that deal with some sort of gas sensor. This makes it virtually impossible to write a review article, completely covering this area. When looking in the scientific literature, summarizing articles can be found that deal with specific application areas or specific types of gas sensors. Examples of review articles about applications for gas sensors are: high volume control of combustibles in the chemical industry [1], exhaust gas sensors for emission control in automotive applications [2,3] or monitoring of dairy products for the food industry [4]. Articles that emphasize a specific type of gas sensor are written about, for example, solid state gas sensors [5], conducting polymer gas sensors using e.g. polyaniline [6], mixed oxide gas sensors [7], amperometric gas sensors [8], catalytic field-effect de-

vices [9] or gas sensor arrays used in electronic noses [4,10]. The review presented here will focus on one specific gas, ammonia.

After a brief introduction of the origin of ammonia in the earth's atmosphere, we consider various artificial sources of ammonia in the air, such as intensive life-stock with the decomposition process of manure, or the chemical industry for the production of fertilizers and for refrigeration systems. Subsequently, different application areas for gaseous ammonia analyzers are investigated with a summary of the ammonia concentration levels of interest to these different areas. Applications in the agricultural and industrial chemistry areas are discussed, as well as environmental, automotive and medical applications for ammonia sensing devices. The overview of application areas provides us with an indication of the required specifications, like detection limits and response time, which will be used as a guideline for the consideration of different measuring principles and techniques, as discussed in the next section.

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## 2. Sources of ammonia

Ammonia is a natural gas that is present throughout the atmosphere. The relatively low concentrations, of low-ppb to sub-ppb levels [11], have been significantly higher in the past. Earth history goes back over 4.5 billion years, when it was formed from the same cloud of gas and interstellar dust that created our sun, the rest of the solar system and even the entire galaxy. The larger outer planets had enough gravitational pull to remain covered in clouds of gas. The smaller inner planets, like earth, formed as molten rocky planets with only a small gaseous atmosphere. It is thought that the early earth formed a chemically reducing atmosphere by 3.8 to 4.1 billion years ago, made up of hydrogen and helium with large concentrations of methane and ammonia. Most of this early atmosphere was lost into space during the history of the planet and the remaining was diluted by a newly forming atmosphere. This new atmosphere was formed mostly from the outgassing of volatile compounds: nitrogen, water vapour, carbon dioxide, carbon monoxide, methane, ammonia, hydrochloric acid and sulphur produced by the constant volcanic eruptions that besieged the earth.

The earth's surface began to cool and stabilize, creating the solid crust with its rocky terrain. Clouds of water began to form as the earth began to cool, producing enormous volumes of rain water that formed the early oceans. The combination of a chemically reducing atmosphere and large amounts of liquid water may even have created the conditions that led to the origin of life on earth. Ammonia was probably a component of significant importance in this process [12–17].

Today, most of the ammonia in our atmosphere is emitted direct or indirect by human activity. The worldwide emission of ammonia per year was estimated in 1980 by the European community commission for environment and quality of life to be 20–30 Tg [18]. Other investigations, summarized by Warneck [11], found values between 22 and 83 Tg. Fig. 1 shows an estimate of the annual ammonium deposition rate

world wide, showing a maximum deposition in central- and Western Europe [11].

In literature, three major classes of current ammonia sources are described [11]. Although the earth's atmosphere comprises almost 80% nitrogen, most nitrogen is unavailable to plants and consumers of plants. There are two natural pathways for atmospheric nitrogen to enter the ecosystem, a process called nitrification. The first pathway, atmospheric deposition, is the direct deposition of ammonium and nitrate salts by addition of these particulates to the soil in the form of dissolved dust or particulates in rain water. This is enhanced in the agricultural sector by the addition of large amounts of ammonium to cultivated farmland in the form of fertilizer. However, when too much ammonium is added to the soil, this leads to acidification, eutrophication, change in vegetation [19] and an increase in atmospheric ammonia concentration [20]. The second way of nitrification is bacterial nitrogen fixation. Some species of bacteria can bind nitrogen. They release an excess of ammonia into the environment. Most of this ammonia is converted to ammonium ions because most soils are slightly acidic [6]. The contribution of nitrogen fixation to the total worldwide ammonia emission is approximated to be 1.0 Tg/year [18].

A larger source in the overall nitrogen cycle is ammonification, a series of metabolic activities that decompose organic nitrogen like manure from agriculture and wildlife or leaves [12]. This is performed by bacteria and fungi. The released ammonium ions and gaseous ammonia is again converted to nitrite and nitrate by bacteria [12,21]. The nitrogen cycle is illustrated in Fig. 2. The worldwide ammonia emission resulting from domestic animals is approximated to be 20–35 Tg/year [11].

A third source of ammonia is combustion, both from chemical plants and motor vehicles. Ammonia is produced by the chemical industry for the production of fertilizers and for the use in refrigeration systems. The total emission of ammonia from combustion is about 2.1–8.1 Tg/year [11].

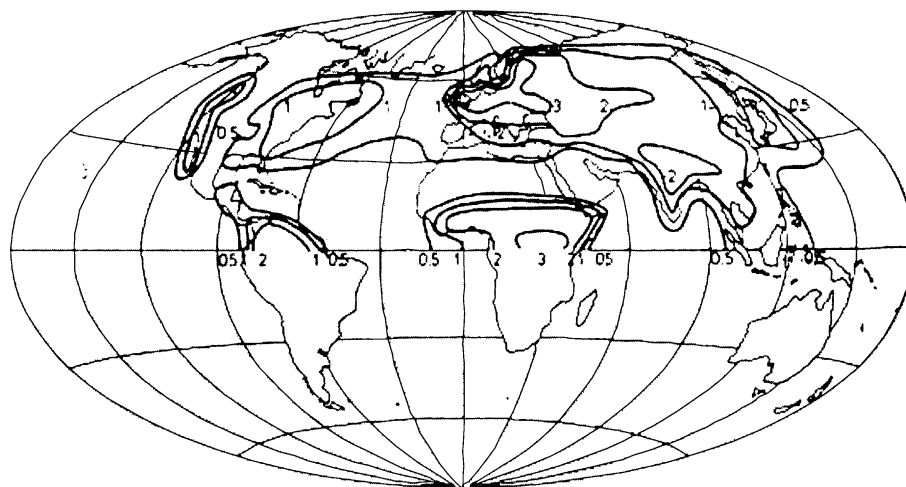


Fig. 1. Annual ammonium deposition ( $100 \text{ mg/m}^2$ ) [11].

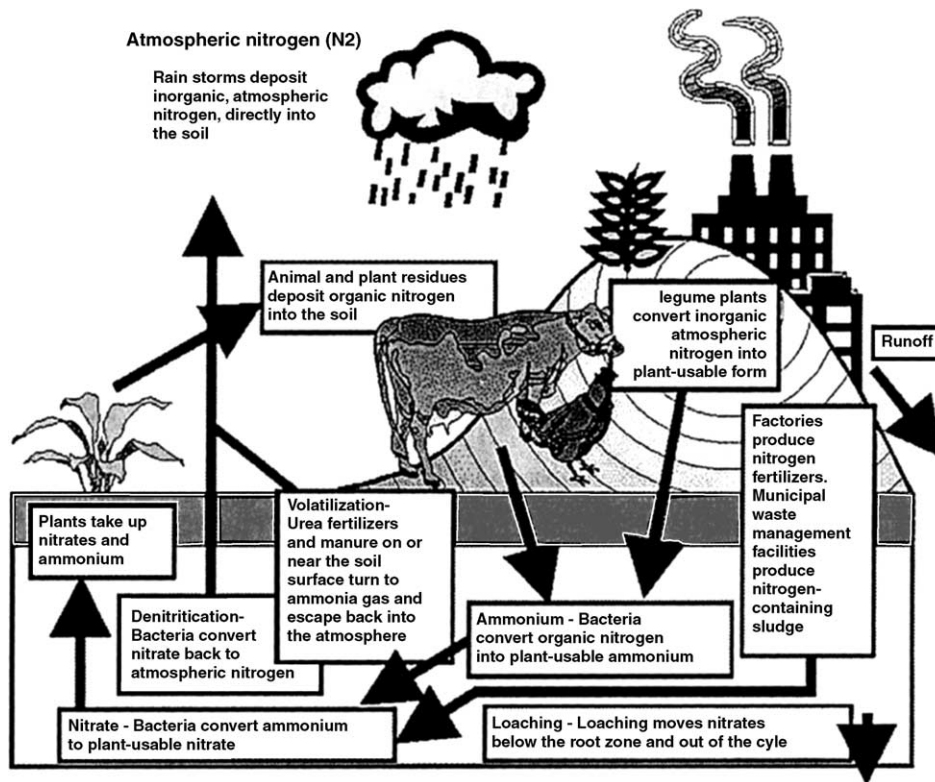


Fig. 2. Nitrogen cycle (Copyright University of Missouri, MU Extension WQ252).

There are numerous smaller sources of ammonia, e.g. surface water. Normally seas and oceans act as a sink for ammonia but occasionally they act as an ammonia source [22,23]. Ammonia is produced because of the existence of ammonium ions that are transformed to gaseous ammonia by alkaline rainwater [23].

### 3. Application areas of ammonia sensors

There are many ways to detect ammonia. High concentrations are easy to detect because the gas has a very penetrating odour. With respect to other odorous gasses, the human nose is very sensitive to ammonia. To quantify the ammonia concentration or determine lower concentrations of ammonia, the human nose fails. However, in many occasions, the ammonia concentration has to be known, even at ultra low concentrations of less than parts per billion in air (ppb) [24]. This section focuses on four major areas that are of interest for measuring ammonia concentrations; environmental, automotive, chemical industry and medical diagnostics, and describes why there is a need to know the ammonia concentration in these fields. Where possible the concentration levels of interest are given for the different application areas.

#### 3.1. Environmental gas analysis

The smell of ammonia near intensive farming areas or when manure is distributed over farmland is very unpleasant.

Furthermore, exposure to high ammonia concentrations is a serious health threat. Concentration levels near intensive farming can be higher than the allowed exposure limit. This results in unhealthy situations for farmers and animals inside the stables, where the concentrations are highest.

Another interesting point is the formation of ammonium salt aerosols. Sulphuric acid and nitric acid react in the atmosphere with ammonia to form ammonium sulphate and ammonium nitrate [25]. These salts are condensation nuclei, forming several nanometre sized airborne particles. Therefore, ammonia reduces the quantity of acids in the atmosphere. These ammonia aerosols have a sun-blocking function, as can often be seen above large cities or industrial areas, as shown in Fig. 3. These clouds of smog have a temperature reducing effect. This effect however, is presently hardly noticeable due to the more intense global warming caused by the greenhouse effect.

Ammonia levels in the natural atmosphere can be very low, down to sub-ppb concentration levels above the oceans. The average ambient ammonia concentration in the Netherlands is about 1.9 ppb. Very accurate ammonia detectors with a detection limit of 1 ppb or lower are required for measuring such concentrations. Near intensive farming areas, ammonia concentrations are much higher, up to more than 10 ppm [26]. It depends on the actual application what concentration levels are of interest. This also determines the time resolution of the required analysis equipment. Monitoring ambient ammonia levels for environmental analysis does not demand



Fig. 3. Smog, or clouds of aerosols, has a sun-blocking effect.

for extremely fast detectors. When an analyzer is used in a controlled venting system in stables, a shorter response time is required in the order of a minute.

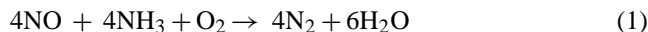
### 3.2. Automotive industry

The automotive industry is interested in measuring atmospheric pollution for three reasons [27]. First, exhaust gasses are monitored because they form the major part of gaseous pollution in urban sites. For instance, ammonia exhaust is associated with secondary airborne particulate matter, like ammonium nitrate and ammonium sulphate aerosols, as discussed in the previous section. Ammonium aerosols are measured to be up to 17% of the particulate matter concentration smaller than  $2.5\ \mu\text{m}$  [27]. Ammonia emissions have been measured up to 20 mg/s or up to 8 ppm ammonia in exhaust gas [28,29].

A second reason for the automotive industry to be interested in detectors for atmospheric pollution like ammonia, is air quality control in the passenger compartment [27]. Modern cars are frequently equipped with an air conditioning system. This system controls the temperature and the humidity of the air inside the car. Fresh air can be taken from the outside of the car or it can be created by conditioning and circulating air inside the car. When there is low quality air outside the car, like air with smoke near a fire or a factory, the system should not take up new air from outside. A major source of unpleasant smell is the smell of manure near farms and meadows. This smell is caused by the increased ammonia concentration in these areas. For indoor air quality monitors, the detection limit should lie around the smell detection limit of about 50 ppm. Moreover, for such an application it is important that the sensor responds very fast. The air inlet valve should be closed before low-quality gas is allowed into the car. A response time in the order of seconds is required.

A third application for ammonia sensors in the automotive area is  $\text{NO}_x$  reduction in diesel engines. Modern diesel engines operate at high air-to-fuel ratios that result in an excess of oxygen in the exhaust gas, resulting in large concentrations of NO and  $\text{NO}_2$  ( $\text{NO}_x$ ) [30,31]. Toxic  $\text{NO}_x$  concentrations are lowered significantly by selective catalytic reduction (SCR)

of  $\text{NO}_x$  with  $\text{NH}_3$ , according to Eq. (1) [32]. Therefore, ammonia is injected into the exhaust system.



It is unfavourable to inject too much ammonia for this is emitted into the atmosphere where it adds to the total pollution, known as ammonia-slip. The injected amount can be optimised by measuring the excess ammonia concentration in the exhaust system. The concentration level that is of interest for this application depends on the controllability of the setup. When the controllability of the ammonia injection is very accurate, the used sensor should be able to measure very low ammonia concentrations in a few seconds. The sensors that are currently used have detection limits in the order of a few ppm [30] and a response time of about 1 min. Because measurements are performed in exhaust pipes, the sensor should be able to withstand elevated temperatures.

### 3.3. Chemical industry

The major method for chemically producing ammonia is the Haber process. The German scientist Fritz Haber started working on a way to produce ammonia in 1904 [33]. In 1918 he won the Nobel Prize in Chemistry for his invention. Ammonia is synthesized from nitrogen and hydrogen at an elevated temperature of about  $500\ ^\circ\text{C}$  and a pressure of about 300 kPa using a porous metal catalyst. The process was scaled up to industrial proportions by Carl Bosch. The process is therefore often referred to as the Haber–Bosch process.

Ammonia production was initiated by the demand for an inexpensive supply of nitrogen for the production of nitric acid, a key component of explosives. Today, the majority of all man made ammonia is used for fertilizers or chemical production. These fertilizers contain ammonium salts and are used in the agricultural sector.

Another substantial part is used for refrigeration. Ammonia was among the first refrigerants used in mechanical systems. Almost all refrigeration facilities used for food processing make use of ammonia because it has the ability to cool below  $0\ ^\circ\text{C}$  [34,35]. The first practical refrigerating machine was developed in 1834 and commercialised in 1860. It used vapour compression as the working principle. The basic principle: a closed cycle of evaporation, compression, condensation and expansion, is still in use today [36].

Because the chemical industry, fertilizer factories and refrigeration systems make use of almost pure ammonia, a leak in the system can result in life-threatening situations. All facilities using ammonia should have an alarm system detecting and warning for dangerous ammonia concentrations. The maximum allowed workspace ammonia level is tabulated to be 20 ppm. This is a long-term maximum and no fast detectors are required, a response time in the order of minutes is sufficient. Especially in ammonia production plants, where ammonia is produced, detectors should be able to withstand



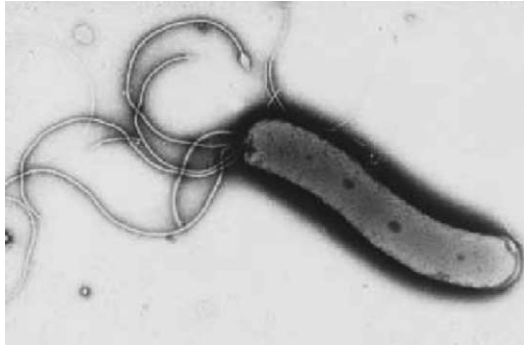


Fig. 4. Electron micrograph of *H. pylori*.

the high temperature, up to 500 °C, applied in the production process.

### 3.4. Medical applications for ammonia sensors

High concentrations of ammonia form a threat to the human health. The lower limit of human ammonia perception by smell is tabulated to be around 50 ppm, corresponding to about 40  $\mu\text{g}/\text{m}^3$  [37]. However, even below this limit, ammonia is irritating to the respiratory system, skin and eyes [38,39]. The long term allowed concentration that people may work in is therefore set to be 20 ppm. Immediate and severe irritation of the nose and throat occurs at 500 ppm. Exposure to high ammonia concentrations, 1000 ppm or more, can cause pulmonary oedema; accumulation of fluid in the lungs. It can take up to 24 h before the symptoms develop: difficulty with breathing and tightness in the chest. Short-term exposure to such high ammonia concentrations can lead to fatal or severe long term respiratory system and lung disorders [40]. Extremely high concentrations, 5000–10,000 ppm, are suggested lethal within 5–10 min. However, accident reconstructions have proven that the lethal dose is higher [41]. Longer periods of exposure to low ammonia concentration are not believed to cause long-term health problems. There is no accumulation in the body since it is a natural body product, resulting from protein and nucleic acid metabolism. Ammonia is excreted from the body in the form of urea and ammonium salts in urine. Some ammonia is removed from the body through sweat glands.

As being a natural body product, ammonia is also produced by the human body [12]. The amount of produced ammonia is influenced by several parameters. For instance, the medical community is considerably interested in ammonia analyzers that can be applied for measuring ammonia levels in exhaled air for the diagnosis of certain diseases [42]. Measuring breath ammonia levels can be a fast diagnostic method for patients with disturbed urea balance, e.g. due to kidney disorder [43] or ulcers caused by *Helicobacter pylori* bacterial stomach infection, of which an image is shown in Fig. 4 [44–46]. For such applications, often only a few ml of exhaled air is available and, at present, no suitable ammonia breath analyzer exists [47].

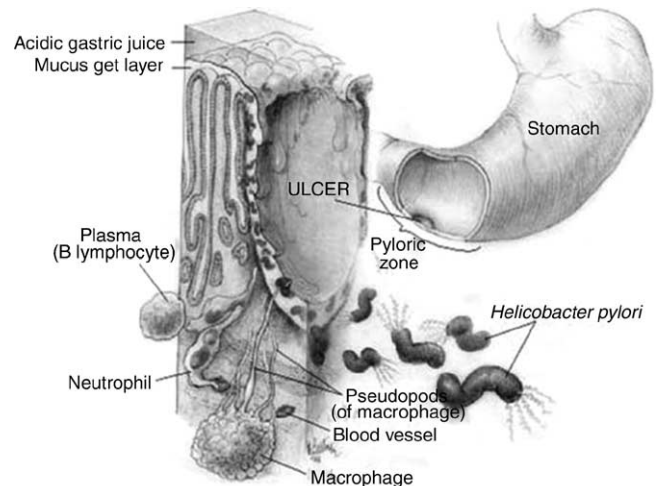


Fig. 5. Immune system cells infiltrate the area of the ulcer to attack the bacteria, leading to inflammation and damage.

After infection, the bacterium penetrates the stomach wall through the mucous barrier used by the stomach to protect itself against the digestive acid gastric juice [45]. The bacterium's most distinct characteristic is the abundant production of the enzyme urease [48]. It converts urea to ammonia and bicarbonate to establish a locally neutralizing surrounding against penetrating acid. This is one of the features that make it possible for the bacterium to survive in the human stomach.

The immune system responds to the infection by sending antibodies [45]. *H. pylori* is protected against these infection fighting agents because it is hidden in the stomach wall protection layer. The destructive compound that is released by the antibodies when they attack the stomach lining cells eventually cause the peptic ulcer, as illustrated in Fig. 5 [45].

The conversion of urea to ammonia and bicarbonate led to *H. pylori* infection diagnosis tests. A first method is based on a gastric  $\text{CO}_2$  measurement, directly related to the bicarbonate concentration. It makes use of an endoscopic procedure [48]. Non-invasive test methods are shown based on measuring exhaled  $\text{CO}_2$  or  $\text{NH}_3$  levels [46,48]. Because the normal exhaled  $\text{CO}_2$  levels are relatively high, isotopically labelled urea is used. Subsequently, labelled  $\text{CO}_2$  concentrations are measured. The results are excellent but the test is expensive and it requires a radionuclide, limiting the applicability. Using a breath ammonia analyzer would be a more appropriate solution. Suitable ammonia analyzers should be able to measure down to 50 ppb ammonia in exhaled air, containing  $\text{CO}_2$  concentrations up to 3% [42]. When measuring in exhaled air, the used analysis equipment should have a reasonable response time of at most a few minutes and often only small volumes of analyte gas will be available.

Ammonia levels in blood are also of interest in the sports medicine. During activity the human body produces ammonia. Ammonia can diffuse out of the blood into the lungs when the ammonia levels become higher than the ammonia levels

Table 1  
Requirements for ammonia analysis equipment in different application areas

Application	Detection limit	Required response time	Temperature range	Remarks
<b>Environmental</b>				
Monitoring ambient conditions	0.1 ppb to >200 ppm [24]	Minutes	0–40 °C	Reduce environmental pollution
Measure in stables	1 to >25 ppm [26]	~1 min	10–40 °C	Protect livestock animals and farmers
<b>Automotive</b>				
Measure NH <sub>3</sub> emission from vehicles	4->2000 g/min [28] (concentration unknown)	Seconds	Up to 300 °C	NH <sub>3</sub> emission is not regulated at this time
Passenger cabinet air control	50 ppm [37]	~1 s	0–40 °C	Automotive air quality sensor mainly aim on NOx and CO levels [26]
Detect ammonia slip	1–100 ppm [29]	Seconds	Up to 600 °C	Control Urea injection in SCR NOx reduction
<b>Chemical</b>				
Leakage alarm	20->1000 ppm [37,40]	Minutes	Up to 500 °C	Concentrations can be very high at NH <sub>3</sub> plants and can even be explosive
<b>Medical</b>				
Breath analysis	50–2000 ppb [42,46]	~1 min	20–40 °C	Diagnosis of peptic ulcer cause by bacteria, small gas volumes

in the air. The expired ammonia levels increase exponential with the workload. The concentration levels of interest, when measuring expired ammonia, are in the range of 0.1 to 10 ppm [38].

### 3.5. Summary of application areas

The application areas that have been discussed in this section are summarized in Table 1. The lower ammonia concentration that is of interest is given as the required lower detection limit. Estimations are given for the required response time and operation temperature.

## 4. Ammonia sensing principles

There are many principles for measuring ammonia described in literature. A different sensor is used in the exhaust pipe of automobiles than for measuring ultra-low concentrations of ambient ammonia for environmental monitoring. The most frequently used techniques in commercial ammonia detectors are discussed in this section. First, metal-oxide gas sensors are described. Secondly, catalytic ammonia detectors are dealt with, followed by conducting polymer ammonia analyzers and optical ammonia detection techniques. In the fifth sub-section, indirect systems using gas samplers and specific chemical reactions to make a selective ammonia analyzer are discussed, followed by a summary of the described techniques.

### 4.1. Metal-oxide gas sensors

The ammonia sensors that have been manufactured in the largest quantities are without doubt metal-oxide gas sensors, mostly based on SnO<sub>2</sub> sensors [7]. A lot of research has been

done on these types of gas sensors [7,49–53], especially in Japan [54]. These sensors are rugged and inexpensive and thus very promising for developing gas sensors. Many models have been proposed that try to explain the functionality of these types of sensors [50]. It is well established by now that the gas sensors operate on the principle of conductance change due to chemisorption of gas molecules to the sensing layer.

A common model is based on the fact that metal-oxide films consist of a large number of grains, contacting at their boundaries [51]. The electrical behaviour is governed by the formation of double Schottky potential barriers at the interface of adjacent grains, caused by charge trapping at the interface. The height of this barrier determines the conductance. When exposed to a chemically reducing gas, like ammonia, co-adsorption and mutual interaction between the gas and the oxygen result in oxidation of the gas at the surface. The removal of oxygen from the grain surface results in a decrease in barrier height [52]. The energy band diagram at the grain boundaries is shown in Fig. 6.

As can be concluded from this model, metal-oxide sensors are not selective to one particular gas. This is a major drawback. Different approaches to make selective sensor systems have been applied [55], like principle component analysis [56], artificial neural networks, also known as the artificial nose [4,10,57] or conductance scanning at a periodically varied temperature [58]. Varying the temperature changes the current density through a Schottky barrier but chemisorption is also a function of the temperature. It is shown that these two effects have a different temperature dependency for different gasses. Techniques have been shown to create micro-machined isolated hotplates that can be used to miniaturize and integrate these types of sensors on a chip [59–61].

A different approach to make selective metal-oxide gas sensors is by using metals or additives that enhance the

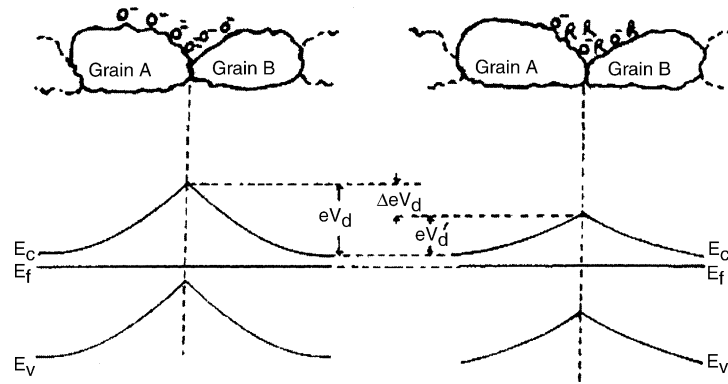


Fig. 6. Energy band diagram showing the Schottky barrier height at the grain boundary of tin oxide without and with a chemically reducing gas [51].

chemisorption of specific gasses.  $\text{WO}_3$  based sensing material is demonstrated to respond to  $\text{NH}_3$  and  $\text{NO}$  [62,63]. Many materials have been added to this sensing material in order to enhance the sensitivity and the selectivity towards these two gasses. The response to the two gasses can be adjusted, as is shown in Fig. 7. Known additives for optimising the ammonia sensitivity of  $\text{SnO}_2$  based ammonia sensors are Pd, Bi and  $\text{AlSiO}_3$  [64] or Pt and  $\text{SiO}_2$  [65].

The lowest ammonia detection limit found in literature is 1 ppm, using a  $\text{WO}_3$  ammonia sensor with Au and  $\text{MoO}_3$  additives. The sensor is operated at an elevated temperature of more than  $400^\circ\text{C}$  [63]. Most sensors have even higher de-

tection limits. Normal detection limits of these sensors range from 1 to 1000 ppm [63,66]. These sensors are commercial available and are mainly used in combustion gas detectors [67] or gas alarm systems, for instance for reliable ammonia leakage detection in refrigeration systems [58]. First air quality monitoring systems for regulating ventilation into the passenger compartment in cars are being implemented.

#### 4.2. Catalytic ammonia sensors

A great number of papers are published about reactivity of catalytic metals to specific gasses, for instance ammonia, hy-

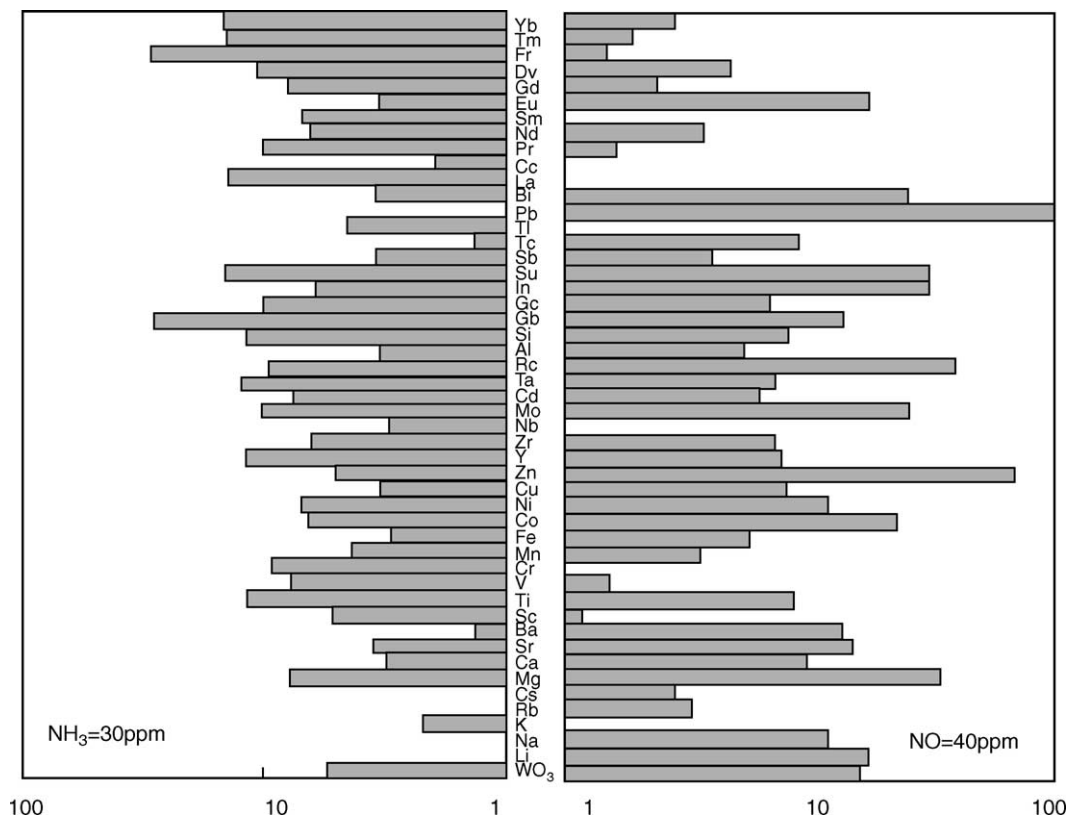


Fig. 7. Sensitivity adjustment of a  $\text{WO}_3$  metal-oxide gas sensor to  $\text{NH}_3$  and  $\text{NO}$  at  $350^\circ\text{C}$  with 1 wt.% additives [62].

drogen, carbon monoxide or organic vapours [9,68,69]. The charge carrier concentration in the catalytic metal is altered by a change in concentration of the gas of influence. This change in charge carriers can be quantified using a field effect device, like a capacitor or a transistor [70,71]. The selectivity of these sensors depends on parameters like the used catalytic metal, the morphology of the metal layer and the operating temperature. Ammonia field effect transistors, gasfets, using a palladium gate material have been shown, resulting in a detection limit of 1 ppm.

The catalytic reaction of a metal layer with gaseous ammonia can also be used in combination with a solid-state ion-conducting material to form a gas-fuelled battery. These gas-sensing systems are known as chemical cells. The catalytic reaction at the sensing electrode will cause a change in electrode potential. The resulting potential difference between the electrode and a counter electrode, over the conducting layer, is used to quantify the gas concentration. These sensors are commercially available for many different gasses. The lower detection limit is normally in the low-ppm range and the accuracy is limited. A chemical cell for ammonia is presented in literature based on an anion-exchange membrane with a Cu electrode and an Ag/AgCl counter electrode [72].

#### 4.3. Conducting polymer gas detectors

A third measurement principle for ammonia makes use of polymers. Different materials have been reported, like polypyrrole [73] and polyaniline [6,74]. The sensing mechanism of polypyrrole films is two-fold: first, there is an irreversible reaction between ammonia and the polymer and, secondly, ammonia can reversibly reduce the oxidized form of polypyrrole [75]. The reduction of the polymer film causes a change in the conductivity of the material, making it a suitable material for resistometric [76] or amperometric ammonia detection [73]. Response times of about 4 min have been shown [74]. The irreversible reaction with ammonia results in an increase in mass in the polymer film. Sensors have been described that detect ammonia using the change in frequency of a resonator, coated with ammonia sensitive polymer [77]. However, the irreversible nature of the reaction causes the sensitivity of the sensor to decrease over time when exposed to ammonia [75]. Although regeneration mechanisms have been proposed, this is a major drawback of this type of sensors [78]. Polyaniline proved to be a much more stable conducting polymer material. The polymer is believed to be deprotonated by ammonia, which results in the change in conduction [79]. The lower detection limit of gas sensors based on the two described polymers is about 1 ppm [74,79]. These sensors are commercially available for measuring ammonia levels in alarm systems.

#### 4.4. Optical gas analyzers

There are two main optical principles for the detection of ammonia described in literature. The first is based on a

change in colour when ammonia reacts with a reagent. With the second principle optical absorption detection is applied as a method to sense gasses.

##### 4.4.1. Spectrophotometric ammonia detection

Spectrophotometry is a technique where a specific reaction causes a coloration of an analyte. The best known example is pH paper. A piece of this paper in a solution colorizes according to the pH of the solution. There are many commercially available detection kits for all kinds of ions and dissolved gasses.

There are different coloration reactions in use for dissolved ammonia. Best known is the Nessler reaction [80]. This ammonia detection method is readily available and applied frequently for determining the total ammonia concentration in water, e.g. in aquaria where too high ammonia levels can cause fish to die. The Nessler reagent consists of dipotassium tetraiodomercurate(II) in a dilute alkaline solution, normally sodium hydroxide. This reagent is toxic. There is not much literature about quantitative measurements with this reaction [81], probably because of the disadvantages. Besides the toxicity, a second disadvantage is the formation of the non-soluble reaction product, a basic mercury(II) amidoiodide [80], making the reaction difficult to implement in a miniaturized detection system.

A second coloration method to measure ammonia concentrations in aqueous solutions is the Berthelot reaction. A combination of ammonia, phenol and hypochlorite results in a blue coloration [82,83]. This reaction uses less dangerous chemicals and the reaction products are all soluble in water. This makes it a suitable technique for integration in miniaturized analysis systems [84]. One drawback of this technique is the rather slow kinetics of the reactions. This was improved by miniaturization in a flow-through analysis system [85]. The detection limit is about 5  $\mu\text{M}$  of ammonia in water or 90 ppb. This technique is still under development in order to lower the detection limit [86].

To improve the sensitivity, the detection limit of the detector has to be improved. This is done by applying different coloration principles, like thin layers of pH indicator [87], fluorescent materials that can be used to label ammonia [88] or a combination of the two [89]. A second option is to apply a very sensitive detection principle, like a photon-counting optical sensor [89] or optical waveguide structures [87] to quantify the coloration, resulting in very sensitive, ppt range, ammonia detectors.

##### 4.4.2. Optical absorption ammonia detection

Optical adsorption spectroscopy is used in the most sensitive and selective ammonia detectors for ambient ammonia. Systems with a detection limit of 1 ppb, that do a full measurement in 1 s, have been reported [90]. Such systems use a laser and a spectrograph. Light travels through air [91] or an ammonia sensitive layer [92,93]. The spectrum of the light reaching the detector is influenced by either the gas composition or the material characteristics as a function of the gas



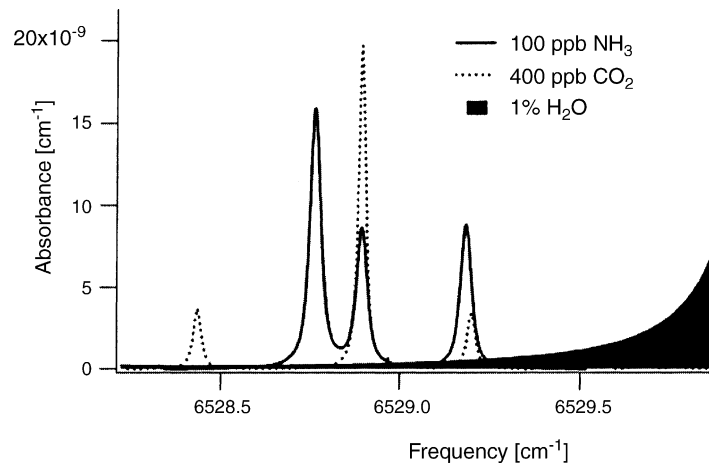


Fig. 8. Ammonia transition at  $6528.76\text{ cm}^{-1}$  [94].

composition. Fig. 8 shows an absorbance spectrogram found in literature that clearly shows that ammonia can be distinguished from interfering gasses, like  $\text{CO}_2$  and water vapour [94]. These systems are used in all kinds of gas analyzers in different application areas. Optical absorbance analyzers that measure multiple gasses are commercially available but cost thousands of dollars.

Although very sensitive and selective ammonia detectors are shown, there are some disadvantages when looking at sensor systems for measuring in small volumes. First, the required equipment is very expensive. It has been tried to use inexpensive diode-lasers to overcome this problem but this also resulted in a decrease in sensitivity [95,96]. Secondly, the sensitivity of absorption spectroscopy is partly determined by the amount of gas between the light source and the detector. For a very accurate analysis the measurement system should be very large. Thus, miniaturization always results in an increase in the lower detection limit. Therefore, this principle is less suited for miniaturized ammonia sensors, e.g. breath analyzers.

#### 4.5. Indirect gas analyzers using non-selective detectors

One major drawback of most available ammonia detection principles is the poor selectivity towards ammonia compared to other gasses. However, it is possible to use a non-specific detection principle, like pH measurement or electrolyte conductivity detection. In that case, the gas analysis system should comprise a selection mechanism that allows only the gas of interest to influence the medium surrounding the detector [24,97]. This can be accomplished by using gas diffusion separation with gas permeable membranes [24,97–99].

These types of air analysis systems make use of gas samplers like denuders or diffusion scrubbers to sample ammonia into a sample liquid [97,100,101]. A major advantage of using gas samplers in ammonia sensor systems is the fact that these systems pre-concentrate the ammonia by sampling a

large volume of the analyte gas into a much smaller volume of liquid, where ammonium ions are formed [102]. Many accurate ways to selectively measure low concentrations of ammonium have been shown [24,98,99].

#### 4.6. Summary of detection principles

The ammonia detection principles that are discussed in this section are summarized in Table 2. The best results found in literature are given for the described detection principles.

### 5. Concluding remarks

Now, the properties of the described sensors and sensor-systems can be compared with the demands of the described application areas, summarized in Table 2. The following conclusions can be drawn:

- Environmental air monitoring systems require a detection limit of less than 1 ppb. Some optical gas sensors are suitable and the indirect method has a sufficiently low detection limit [24,87,90,99]. However, the optical gas sensors are large and expensive, making them less suited. Also the indirect method is rather large and the reagent consumption and maintenance requirements are demanding. A smaller system would be beneficial.
- For measuring in stables, a lower detection limit of 1 ppm is required. All described sensor systems can be applied for this purpose. Sensor equipment that requires much maintenance is inconvenient for farmers. For instance, conducting polymers seems less suited because regular regeneration to prevent loss of sensitivity is required.
- For automotive exhaust applications the required detection limits are not very low, the described sensor systems are all sufficiently sensitive. The elevated temperature in exhaust systems excludes fluidic systems and conducting polymer sensors. Water would evaporate from the fluidic

Table 2  
Parameters of different types of ammonia sensors and sensor systems

Principle	Lower detection limit	Response time	Temperature range	Remarks
Metal-oxide				
WO <sub>3</sub>	1 ppm [63]	~5 min	400 °C	Low selectivity drift
Catalytic metal				
Palladium	1 ppm [70]	~1 min	Up to 600 °C	Low selectivity
Conducting polymer				
Polyaniline	1 ppm [74,79]	~3 min	Up to 150 °C (regeneration)	Irreversible reactions
Optical gas sensors				
Nessler	50 µM (90 ppb) [85]	~1 min	37 °C	For ammonia in water
Coulometric	1 ppt [87]	~5 min		Expensive setup
Absorption spectroscopy	1 ppb [90]	~5 min		Large and expensive
Non-selective detectors				
pH-transitions and EC detectors	100 ppt [24]	~20 min	0–40 °C	Fluidic system

systems and conducting polymers need to be constantly regenerated. The most suitable sensors are metal-oxide and catalytic field effect gas sensors. These types of sensors already work at elevated temperatures and have a sufficiently low detection limit.

- Automotive air quality monitoring systems require very fast sensor systems, responding to increasing ammonia concentrations in a few seconds. None of the described sensors is fast enough.
- Chemical alarm systems do not require sensors that are extremely sensitive and the selectivity is also not that much of an issue. Especially in reactors, the operational temperatures can be elevated. Overall, semiconductor- and metal-oxide gas sensors seem the best-suited type of sensors for these applications.
- A diagnostic breath analysis system for medical ammonia requires a rather low detection limit of 50 ppb. The sensor system should be very selective to ammonia. Furthermore, the system should respond to a change in ammonia concentration within a few minutes. The only ammonia sensors performing to these criteria are optical systems. These systems however, are very large and expensive, making them less suited. The sensitivity and the selectivity of the indirect method are adequate but the system requires too much analyte gas to do analysis in a single breath of air and the system is rather slow. Miniaturization could solve this problem.

## References

- [1] D. Kohl, Function and application of gas sensors, topical review, *J. Phys.* D34 (2001) R125–R149.
- [2] N. Docquier, S. Candel, Combustion control and sensors, a review, *Progr. Energy Combust. Sci.* 28 (2002) 107–150.
- [3] J. Riegel, H. Neumann, H.M. Wiedenmann, Exhaust gas sensors for automotive emission control, *Solid State Ionics* 152/153 (2002) 783–800.
- [4] S. Ampuero, J.O. Bosset, The electronic nose applied to dairy products: a review, *Sens. Actuators B* 94 (2003) 1–12.
- [5] A. Dubbe, Fundamentals of solid state ionic micro gas sensors, *Sens. Actuators B* 88 (2003) 138–148.
- [6] D. Nicolas-Debarnot, F. Poncin-Epaillard, Polyaniline as a new sensitive layer for gas sensors, *Review, Anal. Chim. Acta* 475 (2003) 1–15.
- [7] K. Zakrzewska, Mixed oxides as gas sensors, *Thin Solid Films* 391 (2001) 229–238.
- [8] S.C. Chang, J.R. Stetter, C.S. Cha, Amperometric gas sensors, review, *Talanta* 40 (4) (1993) 461–477.
- [9] I. Lundström, C. Sevansson, A. Spetz, H. Sundgren, F. Winquist, From hydrogen sensors to olfactory images—twenty years with catalytic field-effect devices, *Sens. Actuators B* 13/14 (1993) 16–23.
- [10] D.J. Strike, M.G.H. Meijerink, M. Koudelka-Hep, Electronic noses—a mini review, *Fresn. J. Anal. Chem.* 364 (1999) 499–505.
- [11] P. Warneck, *Chemistry of the Natural Atmosphere*, Academic Press Inc., 1998.
- [12] N.A. Campbell, J.B. Reece, *Biology*, Pearson Education Inc., 2002.
- [13] A.I. Oparin, *The Origin of Life*, Dover Publications, 1938.
- [14] J.B.S. Haldane, *Possible Worlds*, Hugh & Bros, 1928.
- [15] S. Miller, A production of amino acids under possible primitive earth conditions, *Science* 117 (1953) 528–529.
- [16] S. Miller, H. Urey, Organic compound synthesis on the primitive earth, *Science* 130 (1959) 245–251.
- [17] P. Davies, *The Fifth Miracle*, Simon & Schuster, 1999.
- [18] J.R. Iastas, R. de Borger, L. de Temmerman, G. K. Meeus-Verdinne, A. Ronse, P. Scokart, M. Termonia, Effect of ammonia on the acidification of the environment, *European Communities Report No. EUR 11857 EN*, 1988.
- [19] S.V. Krupa, Effects of atmospheric ammonia (NH<sub>3</sub>) on terrestrial vegetation: a review, *Environ. Pollut.* 124 (2003) 179–221.
- [20] D.A. Oudendag, H.H. Luesink, The manure model: manure, minerals (N, P and K), ammonia emission, heavy metals and use of fertiliser in Dutch agriculture, *Environ. Pollut.* 102 (1998) 241–246.
- [21] G.A. Kowalchuk, J.R. Stephen, Ammonia-oxidizing bacteria: a model for molecular microbial ecology, *Ann. Rev. Microbiol.* 55 (2001) 485–529.
- [22] D.S. Lee, C. Halliwell, J.A. Garland, G.J. Dollard, R.D. Kingdon, Exchange of ammonia at the sea surface—a preliminary study, *Atmos. Environ.* 32 (3) (1998) 431–439.
- [23] K. Barrett, Oceanic ammonia emissions in Europe and their boundary fluxes, *Atmos. Environ.* 32 (3) (1998) 381–391.
- [24] J.W. Erisman, R. Otjes, A. Hensen, P. Jongejan, P.v.d. Bulk, A. Khlystov, H. Möls, S. Slanina, Instrument development and application in studies and monitoring of ambient ammonia, *Atmos. Environ.* 35 (2001) 1913–1922.
- [25] C. Baird, *Environmental Chemistry*, W.H. Freeman and Company, 1995.
- [26] G.H. Mount, B. Rumburg, J. Havig, B. Lamb, H. Westberg, D. Yonge, K. Johnson, R. Kincaid, Measurement of atmospheric ammonia at a dairy using differential optical absorption spec-

- troscopy in the mid-ultraviolet, *Atmos. Environ.* 36 (2002) 1799–1810.
- [27] C. Pijolat, C. Pupier, M. Sauvan, G. Tournier, R. Lalauze, Gas detection for automotive pollution control, *Sens. Actuators B* 59 (1999) 195–202.
- [28] T.D. Durbin, R.D. Wilson, J.M. Norbeck, J.W. Miller, T. Huai, S.H. Rhee, Estimates of the emission rates of ammonia from light-duty vehicles using standard chassis dynamometer test cycles, *Atmos. Environ.* 36 (2002) 1475–1482.
- [29] R. Moos, R. Müller, C. Plog, A. Knezevic, H. Leye, E. Irion, T. Braun, K.-J. Marquardt, K. Binder, Selective ammonia exhaust gas sensor for automotive applications, *Sens. Actuators B* 83 (2002) 181–189.
- [30] M. Wallin, C.-J. Karlsson, M. Skoglundh, A. Palmqvist, Selective catalytic reduction of NO<sub>x</sub> with NH<sub>3</sub> over zeolite H-ZSM-5: influence of transient ammonia supply, *J. Catal.* 218 (2003) 354–364.
- [31] X. Xuan, C. Yue, S. Li, Q. Yao, Selective catalytic reduction of NO by ammonia with fly ash catalyst, *Fuel* 82 (2003) 575–579.
- [32] S.G. Buckley, C.J. Damm, W.M. Vitovec, L.A. Sgro, R.F. Sawyer, C.P. Koshland, D. Lucas, Ammonia detection and monitoring with photofragmentation fluorescence, *Appl. Opt.* 37 (No. 36) (1998).
- [33] K.L. Manchester, Man of destiny: the life and work of Fritz Haber, *Endavour* 26 (2) (2002) 64–69.
- [34] A.T. Bulgan, Use of low-temperature energy sources in aqua-ammonia absorption refrigeration systems, *Energy Conserv. Manage.* 38 (14) (1997) 1431–1438.
- [35] P. Colonna, S. Gabrielli, Industrial trigeneration using ammonia-water absorption refrigeration systems (AAR), *Appl. Thermal Eng.* 23 (2003) 381–396.
- [36] J. Fernandez-Seara, J. Sieres, M. Vazquez, Distillation column configurations in ammonia-water absorption refrigeration systems, *Int. J. Refrig.* 26 (2003) 28–34.
- [37] S. Budarvari, et al., *The Merck Index, An Encyclopedia of Chemicals, Drugs and Biologicals*, 12th ed., Merck, 1996.
- [38] L.G. Close, F.I. Catlin, A.M. Cohn, Acute and chronic effects of ammonia burns on the respiratory tract, *Arch. Otolaryngol.* 106 (3) (1980) 151–158.
- [39] C.M. Leung, C.L. Foo, Mass ammonia inhalation burns—experience in the management of 12 patients, *Ann. Acad. Med. Singapore* 21 (5) (1992) 624–629.
- [40] R.E. de la Hoz, D.P. Schueter, W.N. Rom, Chronic lung disease secondary to ammonia inhalation injury: a report on three cases, *Am. J. Ind. Med.* 29 (2) (1996) 209–214.
- [41] R.A. Michaels, Emergency planning and acute toxic potency of inhaled ammonia, *Environ. Health Perspect.* 107 (8) (1999) 617–627.
- [42] W. Ament, J.R. Huizenga, E. Kort, T.W.v.d. Mark, R.G. Grevink, G.J. Verkerke, Respiratory ammonia output and blood ammonia concentration during incremental exercise, *Int. J. Sports Med.* 20 (1999) 71–77.
- [43] L.R. Narasimhan, W. Goodman, C. Kumar, N. Patel, Correlation of breath ammonia with blood urea nitrogen and creatine during hemodialysis, *PNAS* 98 (8) (2001) 4617–4621.
- [44] B. Marshall, J.R. Warren, Unidentified curved bacillus and gastric epithelium in active chronic gastritis, *Lancet* 1 (1993) 1273–1275.
- [45] J.C.E. Underwood, *General and Systematic Pathology*, 2nd ed., Churchill Livingstone Inc., 1996, pp. 414–415.
- [46] D.J. Kearney, T. Hubbard, D. Putnam, Breath ammonia measurement in *Helicobacter pylori* infection, *Digest. Dis. Sci.* 47 (11) (2002) 2523–2530.
- [47] E. Verpoorte, Microfluidic chips for clinical and forensic analysis, *Electrophoresis* 23 (2002) 677–712.
- [48] N.K. Jain, V. Mangal, *Helicobacter pylori* infection in children, *J. Nep. Med. Assoc.* 38 (1999) 140–143.
- [49] G. Sberveglieri, Recent developments in semiconducting thin-film gas sensors, *Sens. Actuators B* 23 (1995) 103–109.
- [50] P.K. Clifford, D.T. Tuma, Characteristics of semiconductor gas sensors I. Steady state gas response, *Sens. Actuators* 3 (1983) 233–254.
- [51] R.K. Srivastava, P. Lal, R. Dwivedi, S.K. Srivastava, Sensing mechanism in tin oxide-based thick film gas sensors, *Sens. Actuators B* 21 (1994) 213–218.
- [52] H.P. Huebner, S. Drost, Tin oxide gas sensors: an analytical comparison of gas-sensitive and non-gas-sensitive thin films, *Sens. Actuators B* 4 (1991) 463–466.
- [53] C. Imawan, F. Solzbacher, H. Steffes, E. Obermeier, Gas-sensing characteristics of modified MoO<sub>3</sub> thin films using Ti-overlayers for NH<sub>3</sub> gas sensors, *Sens. Actuators B* 64 (2000) 193–197.
- [54] N. Yamazoe, *Chemical Sensor Technology*, Elsevier, Amsterdam, 1991.
- [55] J. Mizsei, How can sensitive and selective semiconductor gas sensors be made? *Sens. Actuators B* 23 (1995) 173–176.
- [56] C. Delpha, M. Siadat, M. Lumbreras, Discrimination of a refrigerant gas in a humidity controlled atmosphere by using modeling parameters, *Sens. Actuators B* 62 (2000) 226–232.
- [57] C. Di Natale, F. Davide, A. D’Amico, Pattern recognition in gas sensing: well-stated techniques and advances, *Sens. Actuators B* 23 (1995) 111–118.
- [58] A. Jerger, H. Kohler, F. Becker, H.B. Keller, R. Seifert, New applications of tin oxide gas sensors. II: Intelligent sensor system for reliable monitoring of ammonia leakage, *Sens. Actuators B* 81 (2002) 301–307.
- [59] Cs. Düscö, É. Vázsonyi, M. Ádám, I. Szabó, I. Bársony, J.G.E. Gardieniers, A.v.d. Berg, Porous silicon bulk micromachining for thermally isolated membrane formation, *Sens. Actuators A* 60 (1997) 235–239.
- [60] M. Dumitrescu, C. Cobianu, D. Lungu, D. Dascalu, A. Pascu, S. Kolev, A.v.d. Berg, Thermal simulation of surface micromachined polysilicon hot plates of low power consumption, *Sens. Actuators A* 76 (1999) 51–56.
- [61] F. Solzbacher, C. Imawan, H. Steffes, E. Obermeier, M. Eickhoff, A highly stable SiC based microhotplate NO<sub>2</sub> sensor, *Sens. Actuators B* 78 (2001) 216–220.
- [62] X. Wang, N. Miura, N. Yamazoe, Study of WO<sub>3</sub>-based sensing material for NH<sub>3</sub> and NO detection, *Sens. Actuators B* 66 (2000) 74–76.
- [63] C.N. Xu, N. Miura, Y. Ishida, K. Matuda, N. Yamazoe, Selective detection of NH<sub>3</sub> over NO in combustion exhausts by using Au and MoO<sub>3</sub> doubly promoted WO<sub>3</sub> element, *Sens. Actuators B* 65 (2000) 163–165.
- [64] W. Goepel, K.D. Schierbaum, SNO<sub>2</sub> sensors: current status and future prospects, *Sens. Actuators B* 26/27 (1995) 1–12.
- [65] Y.-D. Wang, X.-H. Wu, Q. Su, Y.-F. Li, Z.-L. Zhou, Ammonia-sensing characteristics of Pt and SiO<sub>2</sub> doped SnO<sub>2</sub> materials, *Solid-State Electron.* 45 (2001) 347–350.
- [66] M. Aslam, V.A. Chaudhary, I.S. Mulla, S.R. Sainkar, A.B. Mandale, A.A. Belhekar, K. Vijayamohan, A highly selective ammonia gas sensor using surface-ruthenated zinc oxide, *Sens. Actuators A* 75 (1999) 162–167.
- [67] A.A. Tomchenko, G.P. Harmer, B.T. Marquis, J.W. Allen, Semiconducting metal oxide sensor array for the selective detection of combustion gases, *Sens. Actuators B* 93 (2003) 126–134.
- [68] P.T. Moseley, Solid state gas sensors, *Meas. Sci. Technol.* 8 (1997) 223–237.
- [69] A. Spetz, M. Armgath, I. Lundström, Hydrogen and ammonia response of metal-silicon dioxide-silicon structures with thin platinum gates, *J. Appl. Phys.* 64 (1988) 1274–1283.
- [70] F. Winquist, A. Spetz, I. Lundström, Determination of ammonia in air and aqueous samples with a gas-sensitive semiconductor capacitor, *Anal. Chim. Acta* 164 (1984) 127–138.
- [71] I. Lundström, A. Spetz, F. Winquist, U. Ackelid, H. Sundgren, Catalytic metals and field-effect devices – a useful combination, *Sens. Actuators B* 1 (1–6) (1990) 15–20.
- [72] N. Mayo, R. Harth, U. Mor, D. Marouani, J. Hayon, A. Bettelheim, Electrochemical response to H<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub> and NH<sub>3</sub> of a solid-state cell based on a cation- or anion-exchange membrane serving

- as a polymer electrolyte, *Anal. Chim. Acta* 310 (1) (1995) 139–144.
- [73] I. Lähdesmäki, A. Lewenstam, A. Ivaska, A polypyrrole-based amperometric ammonia sensor, *Talanta* 43 (1996) 125–134.
- [74] A.L. Kukla, Y.M. Shirshov, S.A. Piletsky, Ammonia sensors based on sensitive polyaniline films, *Sens. Actuators B* 37 (1996) 135–140.
- [75] I. Lähdesmäki, W.W. Kubiak, A. Lewenstam, A. Ivaska, Interference in a polypyrrole-based amperometric ammonia sensor, *Talanta* 52 (2000) 269–275.
- [76] E. Palmqvist, C. Berggren Kriz, K. Svanberg, M. Khayyami, D. Kriz, DC-resistometric urea sensitivity device utilizing a conducting polymer film for the gas-phase detection of ammonia, *Biosens. Bioelectron.* 10 (1995) 283–287.
- [77] Q.Y. Cai, M.K. Jain, C.A. Grimes, A wireless, remote query ammonia sensor, *Sens. Actuators B* 77 (2001) 614–619.
- [78] P. Heiduschka, M. Preschel, M. Rösch, w. Göpel, Regeneration of an electropolymerised polypyrrole layer for the amperometric detection of ammonia, *Biosens. Bioelectron.* 12 (12) (1997) 1227–1231.
- [79] V.V. Chabukswar, S. Pethkar, A.A. Athawale, Acrylic acid doped polyaniline as an ammonia sensor, *Sens. Actuators B* 77 (2001) 657–663.
- [80] A.I. Vogel, *Vogel's Qualitative Inorganic Analysis*, 6th ed., Longman Scientific & Technical, 1987.
- [81] A. Ghauch, J. Rima, A. Charef, J. Suptil, C. Fachinger, M. Martin-Bouyer, Quantative measurements of ammonium, hydrogenophosphate and Cu(II) by diffuse reflectance spectroscopy, *Talanta* 48 (1999) 385–392.
- [82] M.P.E. Berthelot, *Repertoire Chimique Appliquee*1 (1859) 284.
- [83] P.L. Saelle, The Berthelot or indophenol reaction and its use in the analytical chemistry of nitrogen—a review, *Analyst* 109 (1984) 549–568.
- [84] T.T. Veenstra, *MAFIAS—an integrated lab-on-a-chip for the measurement of ammonium*, Ph.D. Thesis, University of Twente, 2001.
- [85] R.M. Tiggelaar, T.T. Veenstra, R.G.P. Sanders, E. Berenschot, H. Gardeniers, M. Elwenspoek, A. Prak, R. Mateman, J.M. Wissink, A.v.d. Berg, Analysis system for the detection of ammonia based on micromachined components modular hybrid versus monolithic integrated approach, *Sens. Actuators B* 92 (2003) 25–36.
- [86] T. Tsuboi, Y. Hirano, Y. Shibata, S. Motomizu, Sensitivity improvement of ammonia determination based on flow-injection indophenol spectrophotometry with manganese(II) ion as a catalyst and analysis of exhaust gas of thermal power plant, *Anal. Sci.* 18 (2002) 1141–1144.
- [87] A. Yimit, K. Itoh, M. Murabayashi, Detection of ammonia in the ppt range based on a composite optical waveguide pH sensor, *Sens. Actuators B* 88 (2003) 239–245.
- [88] N. Strömberg, S. Hulth, Ammonium selective fluorosensor based on the principle of coextraction, *Anal. Chim. Acta* 443 (2001) 215–225.
- [89] A. Elamari, N. Gisin, J.L. Munoz, S. Poiry, M. Tsacopoulos, H. Zbinden, Photon-counting optical-fiber sensor for the detection of ammonia in neurochemical applications, *Sens. Actuators B* 38/39 (1997) 183–188.
- [90] G.H. Mount, B. Rumberg, J. Havig, B. Lamb, H. Westberg, D. Yonge, K. Johson, R. Kincaid, Measurement of atmospheric ammonia at a dairy using differential optical absorption spectroscopy in the mid-ultraviolet, *Atmos. Environ.* 36 (11) (2002) 1799–1810.
- [91] R. Peeters, G. Berden, A. Apituley, G. Meijer, Open-path trace gas detection of ammonia base don cavity-enhanced absorption spectroscopy, *Appl. Phys. B* 71 (2000) 231–236.
- [92] Z. Jin, Y. Su, Y. Duan, Development of a polyaniline-based optical ammonia sensor, *Sens. Actuators B* 72 (2001) 75–79.
- [93] Y-S. Lee, B-S. Joo, N-J. Choi, J-O. Lim, J-S. Huh, D-D. Lee, Visible optical sensing of ammonia based on polyaniline film, *Sens. Actuators B* 93 (2003) 148–152.
- [94] M.E. Webber, M.B. Pushkarsky, C. Kumar, N. Patel, Ultra-sensitive gas detection using diode lasers and resonant photoacoustic spectroscopy, in: *SPIE's International Symposium on Optical Science and Technology*, Paper no. 4817-11, 2002.
- [95] M. Fehér, P.A. Martin, A. Rohrbacher, A.M. Soliva, J.P. Maier, Inexpensive near-infrared diode-laser-based detection system for ammonia, *Appl. Opt.* 32 (12) (1993) 2028–2030.
- [96] G. Modugno, C. Corsi, Water vapour and carbon dioxide interference in the high sensitivity detection of NH<sub>3</sub> with semiconductor diode lasers at 1.5 μm, *Infrared Phys. Technol.* 40 (1999) 93–99.
- [97] S-I. Ohira, K. Toda, S-I. Ikebe, P.K. Dasgupta, Hybrid microfabricated device for field measurement of atmospheric sulfur dioxide, *Anal. Chem.* 74 (2002) 5890–5896.
- [98] G. Schultze, C.Y. Liu, M. Brodowski, O. Elsholz, Different approaches to the determination of ammonium ions at low levels by flow injection analysis, *Anal. Chim. Acta* 214 (1988) 121–136.
- [99] B.H. Timmer, K.M.v. Delft, R.P. Otjes, W. Olthuis, A.v.d. Berg, A miniaturized measurement system for ammonia in air, *Anal. Chim. Acta* 507 (1) (2004) 139–145.
- [100] P.K. Simon, P.K. Dasgupta, Z. Vecera, Wet effluent denuder coupled liquid/ion chromatography systems, *Anal. Chem.* 63 (1991) 1237–1242.
- [101] P.F. Lindgren, P.K. Dasgupta, Measurement of atmospheric sulfur dioxide by diffusion scrubber coupled ion chromatography, *Anal. Chem.* 61 (1989) 19–24.
- [102] C.B. Boring, R. Al-Horr, Z. Genfa, P.K. Dasgupta, Field measurement of acid gases and soluble anions in atmospheric particulate matter using a parallel plate wet denuder and an alternating filter based automatic analysis system, *Anal. Chem.* 74 (2002) 1256–1268.