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Measure Aseptic Tightness During Dynamic Load

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Master Thesis

Measure aseptic tightness during dynamic load

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Abstract

One of Tetra Pak's product segments is food filled packages distributed outside the refrigeration chain. These packages are required to keep the content fresh for a long time, up to a year. To achieve this, the inside of the package must stay aseptic until the consumer opens it. In the distribution chain packages will be exposed to different mechanical loads, such as vibrations, shear forces and various pressure loads. These loads can be either transient or continuous. Ageing and variations in pressure and temperature add additional stresses to the packages. To ensure the aseptic tightness of the packages, tests are continuously performed.

The goal of this master thesis was to find and suggest new or different ways of detecting and measuring leaks. The focus was packages using a mechanical tightening. The use of this type of tightening involves the risk of a temporary leak to appear, if the package is submitted to a load.

The process of gathering information included several brainstorms followed by personal meetings with specialists from different areas. Literature-studies and information from the internet helped sort out and put together a list of ideas. The ideas were evaluated and the most promising were presented as potentially useful to detect temporary leaks. Additionally the practical use of the oxygen measuring equipment, Dansensor 9000, was evaluated. A test was performed where the practical detection limit was found. The equipment was then used to measure the oxygen level in the head space of a new type of package. The aim was to distinguish between diffusion and a present leak but the diffusion rate itself was also of interest.

The use of equipment, based on physical measurements, for detection of small temporary leaks has limitations. Calculations show the existence of a lower detection level that exceeds what is needed to contaminate the content. The report concludes that a gas-sensor mounted inside the package is the method best fitted to fulfil the demands. Statistics and methods involving bacterial growth must be used to fill the gap under the detection limit of physical measurements.

Table of Contents

1 INTRODUCTION

1.1 Background

When transporting filled packages they are exposed to different mechanical loads, such as vibrations, shear forces and various pressure loads. These loads can be either transient or continuous. Ageing, variations in pressure and temperature add additional stresses to the packages. The product-line that concerns packages designed to keep the freshness of the content for a long time, up to a year, have to preserve the aseptic tightness during all of this time. To make sure the packages fulfil the demands of integrity, leak testing is needed. For this purpose Tetra Pak has worked out well-established routines, but new package technologies constantly demands refinement of these. A new type of mechanical tightening introduces the problems involved in finding temporary leaks. To tackle this problem, new or different methods for leak testing have to be found. This constitutes the frame of this master thesis.

1.2 Task

During normal handling at transport and storing there is a possibility for packages with mechanical tightening to open for a finite time and then close again. Existing methods indicates only permanent leaks and are therefore not suited to detect temporary leaks. The task consists of finding and suggesting different methods usable to detect temporary leaks. Throughout this report, reasoning around the mechanical tightening area is based on the design of a certain new package. Other designs exist and all discussions and conclusion might not be applicable for those.

1.3 Objective and limitations

The objectives and limitations of the master thesis are presented below.

Objectives

- Present a wide range of different approaches to solve the problem
- Scan the market to find which ideas that can lead to realistic solutions
- Sort out and present the most promising ideas
- If possible make some initial tests

Limitations

- Due to the limited time frame a full scale test is not possible to perform.
- No method will be fully evaluated.

1.4 Implementation

Several brainstorms were performed to gather information. Literature studies and consultation with specialists both at Tetra Pak and at Lunds Tekniska Högskola helped evaluate the ideas. The internet was scanned to find available equipment to make sure that the ideas could be realized. After a first selection process the most promising ideas was sorted out. All methods are reviewed in the report and suggestions how it is possible to proceed are presented. To properly evaluate a method, testing and validation must be done before it is possible to conclude whether the method will fulfil the needs. This is out of the scope for this master thesis but some initial tests were done with equipment available at Tetra Pak.

2 THEORY

2.1 Nomenclature

2.1.1 Abbreviations and terminology

Accuracy
Defined in the ANSI/ISA—51.1—1979 (R1993) standard Process Instrumentation Terminology as

The degree of conformity of an indicated value to a recognized accepted standard value, or ideal value.

Accuracy is usually expressed as a percent of scale length, common when the instrument is analogue, or as a percent of the reading, common when the instrument is digital. Gas detection knowledge [1].

Aseptic
The word aseptic means the absence of putrefactive microorganisms. Packaging Technology [2].

ASTM (American Society of Testing and Materials)
ASTM international is one of the world largest standards development organizations. Standards for materials, products, systems and services are concerned. ASTM [3].

cfu/ml
A quantification term used to describe the concentration of bacteria in a volume. Cfu stands for “colony forming units” which is the same as viable cells. Chi-square curve fitting [4].

DO-Sensor
Sensor measuring dissolved oxygen in water. Equipment used in this report measures in [mg/L]

Gauge block
Precision made metal or ceramic block, with very high surface finish, used for measuring and calibration.

Leak
A gap or a hole on the package.

Leakage
A flow through a leak.

LTH
Lunds Tekniska Högskola (Lund University, Faculty of Engineering)

Mechanical tightening
When a tightening is solely achieved by adding pressure on two surfaces to press them together, it is referred to as a mechanical tightening throughout this text.

Minimum detectability
Or commonly known as detection level have the following definition according to ASTM.

Method Detection Limit: The minimum concentration of an analyte that can be reported with a 99% confidence that the value is above zero, based on a standard deviation of greater than seven replicate measurements of the analyte in the matrix of concern at a concentration near the low standard.

Or simpler, the detection limit is the lowest concentration of an analyte that can be separated from noise. Gas detection knowledge [1].

Parts per million
The term ppm is used to describe the occurrence of a certain object or substance in relation to surrounding objects or substances. Concerning gases molecules are alluded to but the term can also used to describe the number of failing products in a production chain. One ppm is defined as $1*10^{-6}$.

Parts per billion
This term is unfortunately surrounded with a bit of confusion. The expression billion differs between the United States and Europe. In the US a billion means $1*10^{-9}$ but in Europe it means $1*10^{-12}$. Generally when ppb is referred to nowadays the American interpretation is valid but caution has to be taken.

PIRA
Pira is a commercial consultancy, testing and media business which specialises in retail supply chain technologies related to industries such as packaging, paper etc. PIRA [5].

Precision
Defined by the ASTM as

The degree of agreement of repeated measurements of the same property, expressed in terms of dispersion of test results about the mean result obtained by repetitive testing of a homogeneous sample under specified conditions

Illustrating the difference between accuracy and precision with a dart board would be, if the darts are clustered close together around bulls-eye the thrower has both accuracy and precision but if the darts are clustered somewhere away from the bulls-eye the thrower has good precision but no accuracy. Gas detection knowledge [1].

Resolution
Defined in the ANSI/ISA—51.1—1979 (R1993) standard Process Instrumentation Terminology as

The least interval between two adjacent discrete details which can be distinguished one from the other.

If a measuring stock is divided in millimetres the resolution is millimetres. That means that a given result can be for example 256mm ±1mm, not 256mm ±0.1mm. Gas detection knowledge [1].

Reynolds number
Reynolds number is a dimensionless combination of variables that is important in the study of viscous flow through pipes. Fluid Mechanics [6].

Scalping
Term used to describe the phenomena of how the package material (plastic) affects the content by either absorb or emit flavours. The term is, at Tetra Pak, also used in the context of colours being absorbed by the package material. Blackwell synergy [7].

Selectivity
Selectivity is a term used to describe how good a method can distinguish between different substances, for example gases. The interference from other gases on the target gas

measurement can be expressed as a ratio. Higher ratio means less interference from the specific gas. Electrochemical sensors [8].

2.1.2 Package terminology

Applies to the type of package with mechanical tightening which primarily was used as a reference during this master thesis.

- ***Top***, a package consists of a fibre part and a plastic top. Top referrers to the whole plastic part.
- ***Tightening area***, the area formed when the two surfaces are pressed together.
- ***Headspace***, space not filled with liquid. Can be filled with different gases.
- ***Neck,*** part of the top where the thread is.

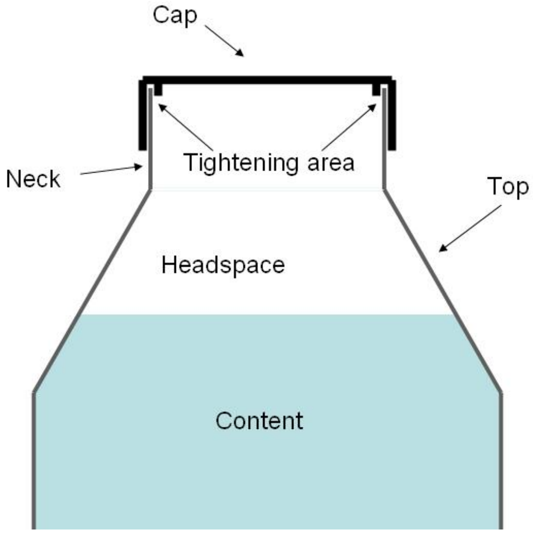


Figure 1 explains commonly used words in the report.

2.2 Problem overview

Historically the closure of semi rigid and flexible aseptic packages has been achieved by heat sealing. Opening this type of packages is done by tearing of a membrane or cut off a piece of the seal. For these packages, the beverage industry has well defined methods of leak detection. When a leak occurs in these packages, it usually remains which makes it detectable. A new problem arose when a package design with mechanical tightening was tried out. A leakage could be temporary, which is very unfavourable considering leak testing and quality assurance. It is better that a package breaks completely and is thrown away, than the scenario that a temporary leak allows bacteria to get inside and cause illness to people.

Before a new product is released in the consumer market it has to fulfil all quality demands. In the case of packages with mechanical tightening there are two aspects to the problem of leak testing. First of all, the package integrity has to be maintained under statically conditions considering mechanical loads. If the package pass this test, solving the problem of detecting a temporary leak is crucial in the decision of whether the product is safe to put on the consumer market.

A primary question is raised, how small leakages can or needs to be detected? It is likely that a leak in a mechanical tightening, depending on the size of the load and how it is applied, can appear in many different geometrical shapes. Differential pressure and the time span of the leakage leads to the possibility for everything from one up to millions of bacteria penetrating the leak.

Consider one bacterium approximately shaped as a sphere with a diameter of 1μm. The fractional volume this bacterium would occupy compared to 1ml is approximately $5*10^{-13}$. This value is far below the detection limit for any existing detection method based on sensors used in practical applications. Bacteria are the major hazard that the package must be capable to resist, consequently the problem has to be solved.

Biotesting is a way to detect small amounts of bacteria. It is explained further under the heading bacteria solutions. Biotesting is unfortunately not the sole answer to the problem because it is a coarse and time consuming method. It is not possible to determine the number of bacteria that actually have infected the content of a package with a reasonable effort. In theory, it is possible to open the package after a specific time, count the bacteria, and with the knowledge of the bacteria reproduction time, calculate the initial amount of bacteria. Other problems involved with biotesting are that the bacteria must be present in the sensitive areas to be able to penetrate the presumptive leak and the need of about two weeks incubation time before a contamination can be proven. Finding another test method that complements the biotest is of great concern.

2.3 Leak properties

When a mechanical tightening is exposed to a rising force, it will be deformed. It is most probable that the deformation at some point will cause a leakage. What is important when developing a new package is that the limit will not be reached during normal handling.

A mechanical tightening in a cap can have different designs, but they are commonly based on a force pressing two surfaces together. The manufacturing method can affect the tightening to a large extent. Test runs of certain types of packages have shown problem when unscrewing the cap. There are forces resisting the shear forces created when trying to turn the cap. These forces might originate from Van der Waal forces caused by wetting. Wetting describes how a liquid behaves when it comes in contact with a solid surface, MIT [9].

However it is commonly known, when two gauge blocks are rubbed together, the only way to separate them by hand is to apply shear forces. This contradicts the fact that it is only Van der Waal forces that fixates the cap. It is possible that small irregularities in surfaces hook in to each other and thereby creates the resisting forces. A possible scenario is, when the package is exposed to a load these forces help keep the tightening intact to a certain level until they suddenly break. The result might be a ketchup effect. This leads to the conclusion, if a leak occurs under these conditions the extent of it will be big enough to measure. On the other hand there might not be any bonds or other forces aiding the tightening. The bonds can break if there is a movement in the material. A small load can be enough. This does not mean that the package start to leak, only that the conditions have changed if it is submitted to another load later.

Due to the problem that all sensor-based measuring have a detection limit above what is needed to contaminate a package, in practice, the answer to the question if a leak occurred would be “yes” or “probably not”, which answers part of the question. Statistics might answer the other part. That is calculating the possibility for the extent of the leakage to be under the detection limit.

It is difficult to foresee the dynamic behaviour of a temporary leak. It is only possible to make qualified guesses.

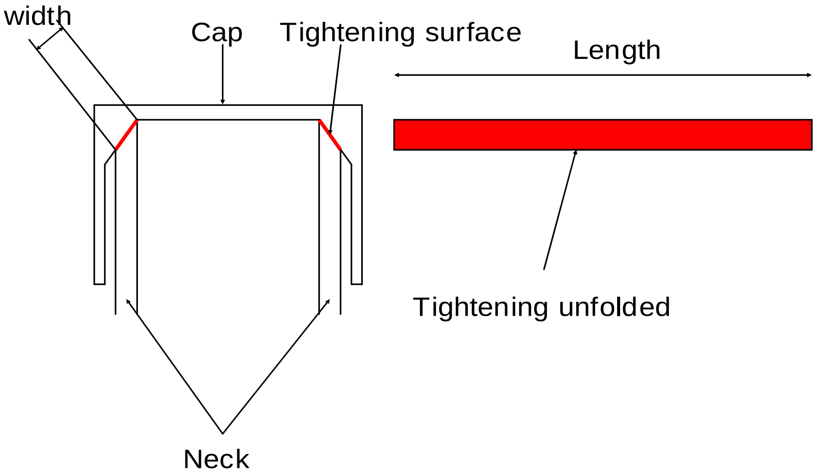


Figure 2 shows the principle of a mechanical tightening on a simplified neck with cap.

Consider the sketch in Figure 2. The width has a great importance for how the leak will take form. If the width of the tightening-surface is small the hole will be quite “straight”, probably oblong. The bacteria will have a shorter path to travel compared to the case where the tightening is wider. On the other hand, due to design, the pressure will be higher between the tightening surfaces when the width is smaller which means that a wider tightening is not necessarily better. With a wider tightening-surface the pressure will be lower between the surfaces. It might lead to enclosures of bacteria if the tightening area partially opens on the outer side and then closes again. If then another load causes the tightening area to partially open on the inner side it can lead to contamination. It seems like the likelihood for these scenarios are small but these kinds of packages shall, besides the distribution procedure, withstand months of storing.

Another interesting issue is if the package is exposed to a compression and a temporary leak occurs. This can lead to the creation of a pressure below atmosphere pressure in the package. Even if the content is not immediately contaminated the lower pressure will facilitate for future contamination. Time and pressure differentials are two very important factors when temporary leaks are considered. Previously performed drop tests show that the duration of the load-cycle can be down to 4ms. This gives a hint about the time span for this kind of loads but other scenarios, like a truck that brakes heavily, will create load-cases with a considerably longer duration.

The pressure differential, the geometrical shape of the leak and the surface finish of the material will all affect the flow through the leak. The flow is assumed to be laminar for permanent leakage. Surface finish of benchmark products and experimental packages has been measured to about 0.25-0.35µm in a pre-study, Ingmar Andreason [10]. Considering a leak to have the form of a small tube it is reasonable to believe that the entering and exit will have no sharp edges. These implications together with some calculations made under the heading “4.1.3 Calculations” and information from the master thesis, “Quantification of critical leak size” [11] leads to the assumption that flow in temporary leaks will be laminar in most cases, only when the diameter of the leak is 2µm or below the flow change to transitional behaviour. In the same master thesis the critical leak size 7µm, for an air filled leak, is established. Critical leak size indicates when microbial penetration into the package is possible. The same report also shows that a leak with a diameter under 2µm will not give raise to a leakage. Compared to a human hair with the approximate diameter of 20µm, this gives a conception of the leak-size needed to jeopardize the integrity of the package. The pressure differential was assumed to not exceed ±34.5 kPa. Quantification of critical leak size [11].

2.4 Measurement options

Leaks have different measurable properties. Each method has limitation and address different problems i.e. is able to measure different quantities. There is no single method that can answer all questions. The categorisation below is based on temporary leaks. The options of measurements are shown below.

Different types of measurement

1. **Indicating that a leak has appeared.** This type of measurement gives no precise information of the extent from the leakage or the exact time and duration of the leakage. Some of the methods in this category might provide some coarse indication of the leak's extent. If a colour indicator is used there can be a noticeable difference in shade of the colour depending on the amount of the substance it has been exposed to.
2. **Measure the quantity of the medium that has leaked in or out of the package.** This is a more precise measurement but still no information of the start time or duration of the leak is available.
3. **Measure quantity in real-time.** Real-time is a relative concept depending on the process and the information required. In this case real-time means that the sample time is short enough to supply information of the start-time and duration of the leak. Uncertainties in form of how the flow affects the possibility to get a stable reading from the sensor complicate the measurement. Information about the dynamical behaviour of the leak could also be deduced if it is possible to compensate for the noise. This type of measurement would make it possible to conclude what caused the leakage if the surrounding also is monitored.
4. **Measure of geometrical leak size.** Information about dynamic behaviour of the geometrical shape of leaks is very hard to obtain. Visual methods or ultra sound could be used. Another way to attack this problem is to calculate the average size of the leak by combining a quantity measurement with the duration of the leak and the pressure differential if this information is available. This can then be used to confirm results from simulations of the dynamic behaviour of leaks.
5. **Indicating where a leak has appeared.** Methods can leave a mark in some way that indicates the position of the leak, which can be observed after a test.

Control volume

Another important issue is where the measurement is done. This affects the preparations of the package, and can also affect the result. The different options are:

A. Inside the package

B. Outside the package

C. Both inside and outside the package

2.5 What loads can a package be exposed to?

It is not within the frame of this master thesis to investigate the load-cases a package can be exposed to, but the subject is of interest because it affects the choice of method to be used for leak testing. It is important that the implementation of the method does not prohibit the possibility to expose the package for different load cases. If all load cases is to be tested the package must be more or less disengaged. A method that only allows the package to be subjected to some of the possible loads is still of interest, but as a complement to other methods.

PIRA is a company that is specialised in package testing, and have studied what loads packages are exposed to from production, through the distribution chain to finally reach the consumer. Different loads packages can be exposed to include, top loads, side compression, vibration, temperature changes, pressure changes, shear forces, drops and compositions of these loads.

3 METHOD AND IMPLEMENTATION

This chapter covers the generated ideas and the selection process. The idea generation process was intended to gather a wide range of ideas covering different disciplines. At every personal meeting, an attempt was made to receive a name of a new person to contact. The reason was to meet many persons with different backgrounds and experiences. All ideas were put together and categorized under the following heading. It must be emphasized that the ideas presented below are taken directly from the idea-generations. Some refinements have been done and information has been added in an attempt to put the ideas in to their context, but there is no guarantee that all ideas can be realized. In the selection process these concerns are taken. There are two reasons for not sorting out some of the ideas at this point. The first reason is, ideas that seem like “science fiction” today might be the ones that solve the problem tomorrow and the second is, the reader might be inspired to come up with new ideas when looking at such imaginative solutions.

3.1 Generated ideas

3.1.1 Bacterial solutions

The use of bacteria for leakage detection can be approached in different ways. A common way is to fill a package with nutritious liquid and apply starving bacteria on the outside. Because the bacteria are starving and can sense “food” in a close range, they will have a desire to reach it. The bacteria can grow inside through a liquid barrier or be flushed in by a flow.

There are some uncertainties when performing this kind of test. It is important, in case of a leak, that the nutritious liquid and the bacteria come in contact with each other if a reliable result is to be obtained. This means that it has to be made sure that the bacteria are present in the zone where a leak can occur. Also the content of the package have to be present in the tightening area. The consequence is that the packages must be kept upside down when conducting the test. Another issue is that bacteria are living organisms that must stay alive to be able o penetrate the package and do harm. If these conditions are not fulfilled it is possible that a leak can occur without being detected. Berit Helmfrid [12]

One of the benefits of using bacteria is that it is a very realistic scenario. The packages are designed to be intact to bacterial contamination. The use of other methods means that a correlation between the measured substance and bacterial contamination has to be made.

The incubation time, when conducting a bacterial test, is usually about two weeks. The content is then analyzed. A special broth called “Mossel EE broth” is used to promote the growth of certain groups of bacteria that contaminates food. After the incubation time, these bacteria can be indicated by a colour shift due to a special procedure when analyzing the sample. This means that they can be it distinguished from other present bacteria and therefore no sterilisation is needed before the test, while other methods might require both the packages and the nutritious liquid to be sterilised. This can be done with radiation-techniques, Mia Ramgren [13]. Condalab [14]

3.1.1.1 Bacteria Immersion

This is a well known method. It is performed by filling a package with nutritious liquid and immerse it in a bath containing bacteria. To adjust the method to detect temporary leakages, the package can be exposed to loads when being immersed in the bacteria bath. Quantification of critical leak size [11] and Nelsonlab [15].

3.1.1.2 Bacteria specific placement

A further elaboration of the bacteria immersion method is to inject the bacteria in the threads between the cap and the neck. This means that the package do not have to be immersed in a bath of bacteria. The benefit is that a smaller quantity of bacteria can be used and the package is easier to handle. The test becomes more reliable when more realistic loads can be applied. The use of fewer bacteria also improves the working environment. The bacteria-solution can be injected either through a pre-made hole in the cap or from the lower tightening between cap and top.

3.1.1.3 Bioaerosol

Information about aerosols, see heading “Aerosol, solid/gas”. Bacteria in aerosol form, referred to as a bioaerosol, can be used as an alternative to immersion. The principle is the same as for immersion, using a package filled with nutritious liquid. The aerosol is forced on the package in a flow (spray). An advantage is the possibility to freely expose the package to loads. It has been shown that aerosol tests are more sensitive than immersion tests. Quantification of critical leak size [11] and Nelsonlab [15].

3.1.1.4 Dormant bacteria

Some bacteria families, for example Bacillus and Clostridium, can develop a dormant stage, called endospore, when conditions for reproduction are bad. The endospore can remain for thousands of years and then transform to a bacteria when living conditions are better. ”Livets pigment: om de viktiga hemmolekylerna” [16]

This method is based on the idea of filling a package with endospores. The substance needed to make the endospores transform to bacteria is oxygen. A study of the content would reveal a leakage if bacteria is indicated. The requirement to make this method work is that the oxygen level in the package is kept on a low level before a leak occurs. Mia Ramgren [13].

3.1.2 Chemical solutions, visual reactions

The methods under this heading are based on the idea that a chemical reaction leaves visible traces. The reaction can result in a change of concentration, colour, pH, temperature etc. The only restriction is that the reaction leaves a visible trace like colour, soot, smoke, bubbles, burning or corrosion. Only imagination limits the number of possible method sorting under this category. Three different ideas, picked from the brainstorms, are covered here.

3.1.2.1 Colour indicator

If a pad is attached in the cap it would be visible through the surface if the cap-material is transparent. The pad can be produced in such way that makes it sensitive to a certain gas, for example by mixing a substance, that strongly reacts with chosen gas, with a polymer. If the reaction leads to a colour change of the pad it can be used to indicate a leakage.

3.1.2.2 Burning

If the package is filled with a gas that is ignitable, applying a spark outside the cap would lead to a flame if a leakage occurs. This might also be achieved with a reaction between two gases or a gas and another substance. The reaction can be visible in form of a flame, traces of soot or defects on the surfaces.

3.1.2.3 Colour indication with enzymes

An enzyme is an example of a protein where the function is dependent of its shape. An enzymes active area has a very precise shape that combines with a specific substrate-molecule. A catalyst is added to start the reaction. The basic idea of this method is to fill a package with liquid containing enzymes. If a leakage occurs, oxygen enters the package and reacts with the enzyme which leads to a colour change of the liquid.

Propose of reaction.

$$\text{Glucose} + O_2 \xrightarrow{\text{Glucose oxidase}} \text{Gluconolactone} + H_2O_2$$

$$H_2O_2 + \text{Substitute} \xrightarrow{\text{Peroxidase}} \text{Coloured product}$$

Patrick Adlercreutz [17]

By changing concentrates of the components the sensitivity of the method can be altered. By changing temperature the process can be speeded up. Enzyme-activity increases up to an optimal temperature, 50-70°C depending on the enzymes. The maximum temperature must not be exceeded because the enzyme will then denaturise and change shape. Helix-I bioteknikens tjänst [18].

The method can be enhanced with a mirror in the bottom to reflect light for detection of a colour-change with a photo-sensor. Personnel at LTH, biotechnology department have claimed to be able to help realize this method.

3.1.3 Chemical solutions, measurable reactions

Sometimes a chemical reaction can lead to the possibility of measuring a quantity. It can be a change in properties, production of a bi-product or reagents combining to a new substance. Different sensors are then used for the detection.

3.1.3.1 Citrus acid / pH-reactant

The pH value is a measure of the acidity or alkalinity of a solution which is tied to the activity of the hydronium ions. Different sensors and indicators for measurement of pH-levels are available. One of the good pH measuring systems found on the market have measuring range between -2.000 – 19.999, see Schottinstruments [19].

A way of utilize pH-changes in reactions is to fill a package with a pH-reagent and keep an acid, for example a citrus acid, outside the tightening. Also different substances in gas form have the ability to affect the pH value. A leakage would be detected when the sensor detects a change of the pH value in the package.

3.1.3.2 Baking powder/vinegar

Baking powder (sodium hydrogen carbonate) and vinegar (acetic acid) react with each other and releases carbon dioxide. The carbon dioxide that is released can be measured with a CO_2 -sensor.

One way to implement this idea is to place baking powder dissolved in liquid in the threads, close to the tightening, between the neck and the cap. The package can be filled with vinegar and a CO_2-sensor, mounted inside, would log the changes of CO_2 concentration in case of a leakage.

Baking powder		Vinegar		Sodium acetate		Water		Carbon dioxide
$NaHCO_3$	+	CH_3COOH	→	CH_3CO_2Na	+	H_2O	+	CO_2

Colorado University [20].

3.1.4 Colloids

A colloid system is a heterogeneous mixture of two separate phases, one dispersed and the other continuous. The phases can be gas, liquid or solid, but both can never be in gas phase concurrently. The dispersed phase can have particles as small as 1nm and up to 1μm. National Encyklopedin [23] and “Answers” [21]

3.1.4.1 Aerosol, solid/gas

Aerosols are mixtures of particles and gas. The particles can be either solid or liquid and they range between 10nm to several tens of μm in size. The particles have such a small mass that the gravity is not the most influencing force, and thereby the particles float freely in the gas. Smoke is an example of an aerosol. One big advantage with aerosols compared to gases is that they do not diffuse through materials.

Aerosols can as mentioned before be sprayed against the package in form of bioaerosol but under this header the approach is to fill a package with the aerosol. Depending on the aerosol, different methods can be used for detection. A coloured smoke could be used, similar to one used for a smoke grenade. The leakage could be detected visually by traces on the tightness area. If the particles in the aerosol are metallic a metal detector can be used for detection. Earth Observatory [22].

3.1.4.2 Ferrofluid (Magnetic fluid), solid/liquid

Ferrofluid is a colloid system that consists of a liquid carrier and magnetic nanometre-sized particles coated with a surfactant to prevent the particles to agglomerate. The properties of ferrofluid can be substantially changed if a different liquid carrier is used. The capacity for a liquid to penetrate a small leak depends to a high grade of the viscosity and surface tension. It has to be checked that it is possible to manufacture a ferrofluid that fulfils the needs.

One way of using ferrofluids can be to fill a package with ferrofluid and have a magnet or a magnetic recorder placed on the outside of the cap. If a leakage appears, it would be detected either by the liquid getting stuck on the magnet or recorded by the recorder. An inductance sensor can also be used to observe any leakages of the ferrofluid.

Another approach is to trace ferrofluid that has leaked out by exposing it to either ultrasound or microwaves. This would cause a movement of the particles and thus a temperature rise. A heat camera could be used to detect the differences in temperature. National Encyklopedin [23].

3.1.5 Electrical solutions

3.1.5.1 Electrical measurement with conducting medium

This method is an existing method to measure permanent leaks that can be further elaborated to measure temporary leakages. The method is based on an electric circuit that closes if a leakage appears.

The test package is filled with a conducting medium connected to one of the poles in a circuit. The package is then immersed into a container with a conductive medium connected to the other pole in the circuit. If a leak appears the electric circuit is closed and a current can be detected, see Figure 3. There is a possibility to keep liquid between the threads connected to one side of the circuit.

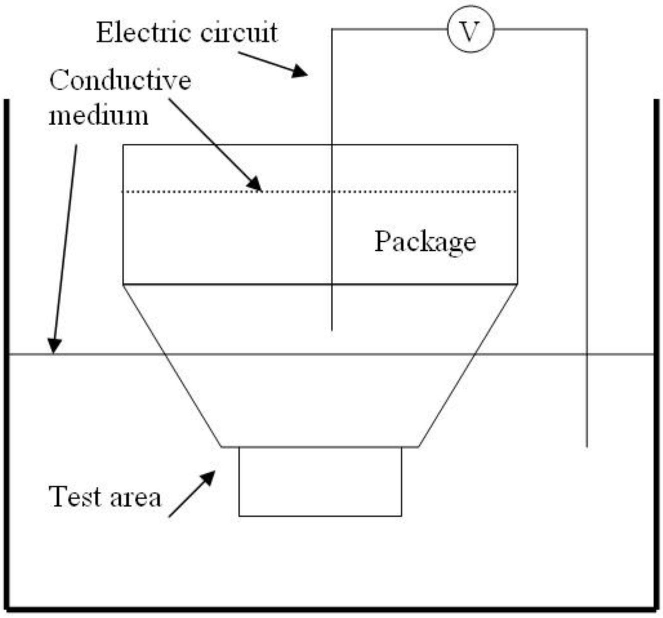


Figure 3 shows the basic functions of measuring with conducting medium.

3.1.5.2 Electrical conductivity

The conductivity of a material, which is a measure of the ability to conduct an electric current, changes with the composition. Deionised water, or other liquids, can be used to indicate this change. If the deionisation level in the liquid is altered this leads to a change in conductivity. Normal air, which contains oxygen, would accomplish this and a leak can thereby be found. A conductivity sensor mounted inside the package detects the change and transfers the data wireless to a receiver outside.

3.1.6 Footprint

As the name purposes the idea of footprint methods is to get a permanent mark after a leakage. The mark can arise from coloured liquids, colloids, scalping or other substances. Colloids are treated by their own under the heading “colloids”.

3.1.6.1 Coloured liquids

Coloured liquids, usually dye, are frequently used for leak detection. The idea is to discover a leakage through visual inspection outside the tightening. Important properties of the liquid are penetration ability and colour intensity. According to NDT [24], the eye detection limit is approximately 70-80 µm which makes small leaks invisible for the eye. It is therefore important that the dye spreads to the surrounding area in order to enlarge the visible tracks of the leakage.

3.1.6.2 Scalping

Scalping is a phenomenon where the flavour or colour of a substance is absorbed by the package material. If the package is filled with a liquid that have a high scalping potential for the plastic material in the top or cap, a leakage can leave visible marks in the tightening. The advantage of this method is the possibility of unscrewing to cap without destroying the signs from the leakage.

3.1.6.3 Liquid collector at tightness area

The idea is based on that a small capillary tube is placed in connection with the tightening area. The purpose of the tube is to collect a liquid originating from a leakage in order to visualize it.

3.1.6.4 Traces from medium

The idea of this method is based on adding a material, for instance a powder, above the tightening area before production. The medium inside the package can be of a kind that reacts strongly with the added material and thus creates cracks or other traceable marks.

3.1.7 Gas detection

The need of detecting hazardous gases or the lack of oxygen has an old tradition in the mining industry. In the beginning birds together with oil lamps served as the first gas sensors. The birds died before humans of toxic gases and the light died when the oxygen disappeared. The development of gas sensors has taken big steps since then and is nowadays used widely in industry and many other places for detection and measuring of gases. References for each section in this chapter are placed in the end of the section, and references concerning the whole gas detection-chapter are placed in the end of the chapter.

3.1.7.1 Tracer gases

There are a wide range of gases that are possible to use in leak detection. Most are toxic but can be used in sealed chambers. Helium and Hydrogen are examples of non toxic gases that could be used as tracer gases in sealed chambers. They are both constituents in ambient air but only in very low concentration which means that if they are going to be used as tracer gases the concentration must be altered by supplying gas from an external source.

A difficulty has been noticed when trying to find sensors or other equipment to measure certain types of gases. Lack of commercial interest or better options available are probable reasons.

Usually a low concentration of the tracer gas gives best functionality. Many gas detection devices have best accuracy at low concentration levels. A low concentration gradient will also make the test less sensitive to the error from diffusion. Using a gas that is not a constituent of air will assure that the concentration inside the package is zero from the start thus making it easier to reveal a permanent leak. When considering temporary leaks it depends of the amount of gas leaking in and the sensitivity of the equipment. All gases that not exist as natural constituents of ambient air have the big disadvantage that the surrounding environment has to be controlled. Another issue on this subject is that the sealed chamber has to be big enough to house the testing equipment used to create the loads.

Considering gases present in ambient air, tests can be performed almost anywhere. The largest constituent, Nitrogen, could be a suitable tracer-gas but it is hard to find hardware for detection. One reason is probably the properties of being a harmless and at low temperatures inert gas that leads to the lack of commercial interest. Oxygen detectors on the other hand are widely used for leak detection. The car industry has a great interest in measuring Oxygen in combustion engines which aids the research and development in this field.

Argon is mostly used as background-gas in gas detection applications. It is hard to find equipment used for Argon detection solely but this option can not be ruled out. Often it is possible to buy equipment tailor-made for the application. In some cases equipment used to measure a certain type of gas can calibrated to be sensitive for another kind of gas.

Carbon dioxide is used in some leak detecting applications but in these cases the package is filled with CO_2 and the equipment detects gas leaking out of the package.

When handling gases in leak detection tests there are a few things that have to be considered. The molecular mass and viscosity of the gas affects the flow in leak. In the applications investigated here this will probably not be a problem. Calculations show that the flow encountered will be laminar. If the gas that is used have a high molecular mass or low diffusion coefficient precautions against stratification might have to be taken, for example mixing the gases before measuring.

Hazards involved in gas testing include flammability, explosion risk, intoxication and asphyxiation. Precautions have to be taken. Today environmental aspects are very important, storing or disposing substances that are ecologically harmful can result in high cost. Nondestructive test handbook [25].

The Composition of air.

Gas	***Symbol***	***Percent by volume***
Nitrogen	N_2	78,084%
Oxygen	O_2	20,9476%
Argon	Ar	0,934%
Carbon Dioxide	CO_2	0,0314%
Neon	Ne	0,001818%
Methane	CH_4	0,0002%
Helium	He	0,000524%
Krypton	Kr	0,000114%
Hydrogen	H_2	0,00005%
Xenon	Xe	0,0000087%

Table 1. Composition of air at sea-level in percent by volume at 15°C and 101325Pa pressure. Table is from Physlink [26]

3.1.7.2 Different methods

The focus when examining gas detection methods is that the measuring takes place inside a sealed/tightened package i.e. the problem is to detect whether a gas has entered the package. It is possible to reverse the problem but then with the restrains that the surrounding environment always has to be controlled and it is only possible to assume that the detection of gas leaking out of the package indirectly means that gas also have had the possibility to enter the package. When measuring gas inside a package there are four different methodologies used to approach the problem, which all the methods sorts under. The four methodologies are covered one by one in the following text.

3.1.7.2.1 Sensor mounted inside the package

In many packages there is enough space to place a sensor inside of it. There is a variety of different sensor on the market and new kinds are continuously developed. It is possible to measure traces of gas in the headspace or a specimen of gas dissolved in fluid. With a wireless transmitter the package can be handled more freely when exposing it to different robustness tests. If a wire connection is needed, the setup probably has to be stationary. This method can also be used as laboratory method with the sensor mounted on a fixture that makes it possible to test different parts of the package, see Figure 4. The advantage with this method is that several measurements can be made under a long time period without affecting the conditions inside the package. Depending of the sensor, the measurements can take place more or less continuously thus making it possible to monitor the time for when the leak appeared. This makes it more likely to detect a temporary leak. A disadvantage is that the packages have to be specially prepared before measuring.

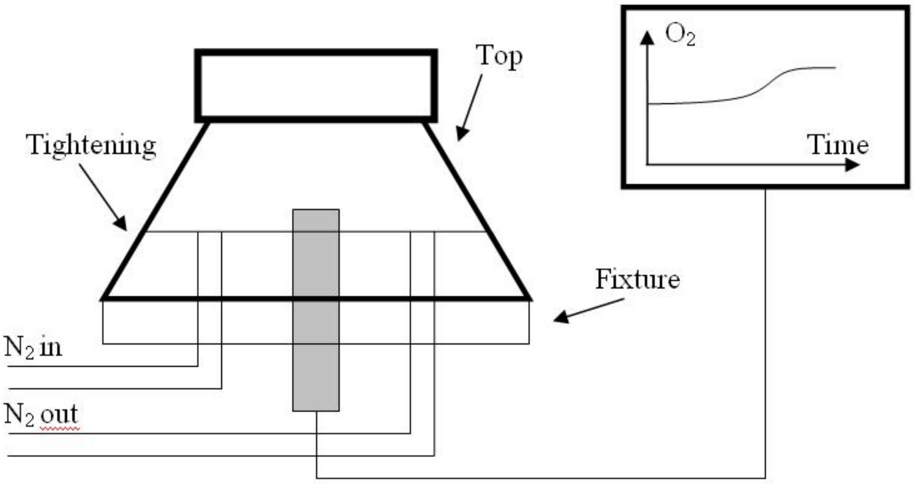


Figure 4. Example of principle for measuring oxygen concentration with an O_2-sensor in a laboratory environment. The Nitrogen is used to flush the headspace free of oxygen.

3.1.7.2.2 Measuring traces of gas in a flow

This is a less flexible method of leak testing. Two holes have to be made in the top-surface when measuring inside the package. Tubes or pipes are connected to the holes and a gas flow is led through package in to the analyzing equipment. This restrains the portability which makes the method most suitable for detecting permanent leaks or establishing diffusion rates, though it is possible to do robustness tests in some extent. One way is to have the package fixated in a fixture and expose the cap for different loads, see Figure 5.

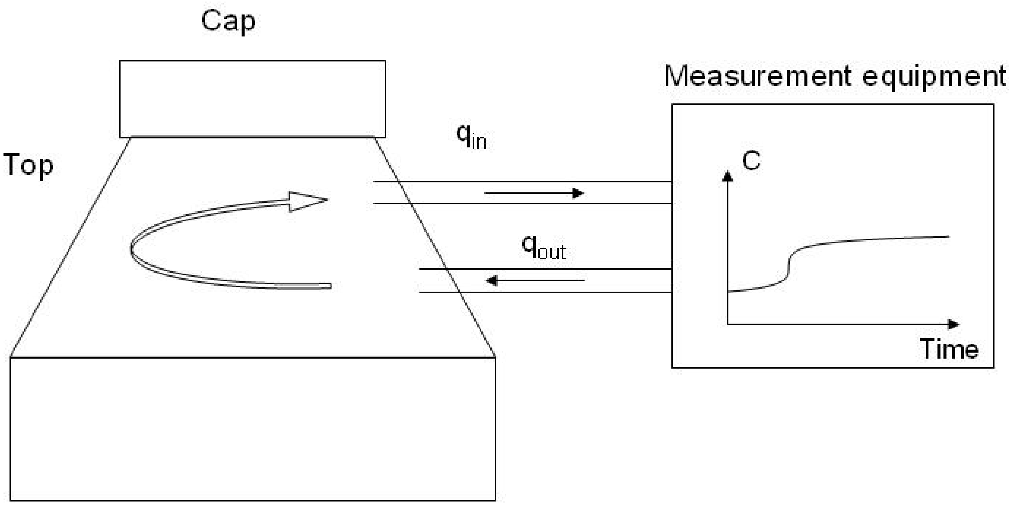


Figure 5. Principle for measuring gas concentration in a flow.

3.1.7.2.3 Extract sample for analyze

This method is based on extracting a gas sample from the headspace with a syringe. The advantage of this method is that the test samples are free to handle and no equipment is mounted inside the package. It is possible to take products directly from the production for testing but the option to alter the composition of the gases in the headspace for laboratory tests remain. To extract a sample a syringe is inserted through the wall of the package, see Figure 6. Normally only one measurement can be performed due to the leak around the syringe, but using a septum might make it possible to take more than one sample. This can lead to a problem though. Taking a sample means that a small volume of gas mixture is extracted and thus the conditions in the package are altered. This will affect the result for the following samples. The difference in concentration can be compensated but the problem is that the pressure will be lower inside the package than outside after extracting the sample. An under-pressure will facilitate for gas to penetrate the package thus destroying the significance of the test. The fact that it is not possible to take two or more samples without affecting the result means that the initial conditions in the package is not known. Then the test has to rely on the fact that the same initial condition can be reproduced and statistically significant. If a temporary leak is to be found, then a tracer gas that is not a constituent of ambient air might be more suitable. In that case the initial conditions are known which makes it easier to establish that a leak in fact has occurred. The drawback is that the surrounding environment has to be controlled.

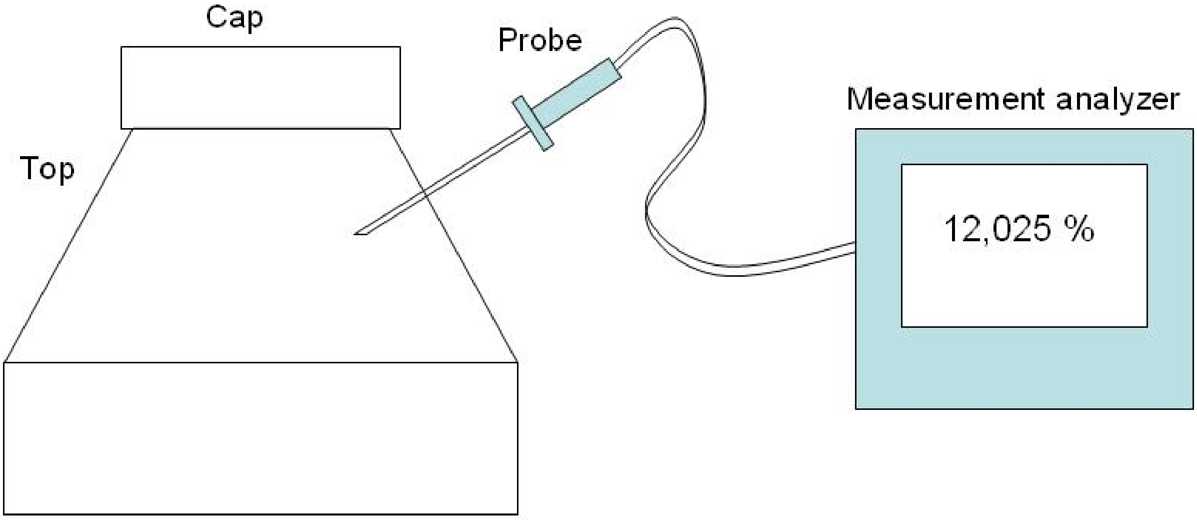


Figure 6. Principle for measuring gas concentration by extracting a sample for analyzes.

3.1.7.2.4 Measuring with radiation

The common principle for these methods is that radiation is directed through or in to a package, usually electromagnetic radiation in the form of laser light. One technique is based on radiation directed into the package and reflected by the inner walls or a mirror mounted inside the package and then collected at the same place from where the radiation is emitted. A second technique involves placing a helping device inside the package. The device can, for example, be a small pad that reacts to the concentration of a certain gas. When exposing it to led light or laser light radiation will be emitted with an intensity related to the gas concentration. Collecting the emitted light will provide the measurement. Problems involved with this kind of measurement are that the package usually needs to be transparent in some extent. The advantage with this type of method is that several measurements can be made on a package without affecting it. It can also be used for products in production. It is portable and can be used on a large number of packages. This is a very attractive method. The problem is that the only products found on the market are of the kind that utilises a pad inside a package and they do not have the resolution acquired.

3.1.7.3 Different methods of detection

The following sections will cover a wide range of different technologies used in gas detection applications. As this is one of the most promising areas, an extra effort to really reach out to the outskirts of the subject has been made in this section. One of the interesting things about sensors is the variety of different techniques. Many of them can be tailor-made for a specific application. Hopefully this section can be inspiring when future test methods are to be found. A parallel to the concept of “mechatronics” would be to integrate the sensor in the package. This can, for example, be done in the form of a conductive polymer coating. The heading “Emerging techniques” is included to provide search words on the internet, it is found in appendix. The methods are still in the research state but excluding them from the report could lead to missing vital information.

3.1.7.3.1 Gas detection with sensors

The following section covers some of the existing methods of gas detection with sensors. A sensor is a device that responds to a physical stimulus and emits a resulting signal. The signal is received, either with a wire or wireless, by a transmitter that processes the signal. Sensors are usually small although the definition doesn’t say anything about size. This means that they are possible to mount inside a package. Sensors can also be mounted in equipment that needs to extract a sample of the gas for analysis. Depending on the type, sensors can provide measurements of gas concentrations both in gas form and dissolved in liquid. Sensor applications in this field cover a wide area. Besides all existing techniques there is a broad research in enabling techniques. A desired solution with a sensor would be to mount a small accurate sensor on a transmitter-card that sends all information about the gas concentration wireless in real time. MNT, Gas Sensor Technology [27].

3.1.7.3.1.1 Electrochemical sensors (wet electrolyte)

Working principle:

The target gas reacts chemically at the surface of the sensing electrode that is enclosed in a fluid electrolyte. The reaction is either an oxidation or a reduction that is catalyzed by the electrode material specially developed for the target gas. Through the reaction a current is produced that is directly proportional to the concentration of the gas present.

General overview:

This type of sensors can be used to measure a wide range of gases. When looking at different qualities like life expectancy, selectivity and good reliability the electrochemical sensors perform best when measuring oxygen. On the other hand the resolution and detection level is generally much better when measuring toxic gases like CO and NOX. Big efforts are made to develop and improve this kind of sensors which probably will result in better resolution for oxygen measurements. If toxic tracer gases are considered this type of sensor is sufficient right now. Sensors with detection limits down to 0.6 ppb, when measuring ozone, are available. The fact that electrochemical sensors have the lowest power consumption among all gas detectors make them suitable to be mounted inside packages for long-time tests. The sensors are minimally affected by pressure changes but sensitive for temperature changes. Usually the temperature variations are internally compensated for but the problem should be considered if the tests involve big differences in temperature. The price for these types of sensors is usually low. An interesting alternative provided by Teledyne, is based on a electrochemical sensor mounted in a sample extracting equipment. The equipment has a detection level of 0.5ppb. The resolution is incredible 0.1ppb.

Measurable gases:

Ammonia, arsenic hydride, bromine, carbon monoxide, chlorine, hydrogen, hydrogen chloride, nitrogen dioxide, oxygen, ozone, etc.

International Sensor Technology [8], City Technology [28], Auburn University [29] and Teledyne[30]

3.1.7.3.1.2 Zirconium oxide sensors (solid electrolyte)

Working principle:

Zirconium oxide is used as a solid state electrolyte with platinum plates or thin Palladium coating on opposing sides. The platinum plates serve as electrodes. One electrode is exposed to a reference gas, typically air, and the other to the sample gas. Heating of the electrolyte above 450°C will results in vacancies in the ceramic lattice. Oxygen ions thereby can move across the solid thus creating a current. This current is a function of the difference in oxygen concentration on each side of the electrolyte.

General overview:

Zirconium sensors have a good response to low levels of oxygen if no reducing gases, like CO, are present in the sample gas. They work well over a wide range of oxygen concentrations, from ppm (ppb levels when measuring dissolved oxygen in liquids) levels to

100%. The response time characteristics are excellent and the accuracy is 5ppm. There are though some problems with this kind of sensor. The fact that it is heated to high temperatures every time a measurement is made shortens the lifetime. Usually the sensor head last for up to a year before it has to be replaced but can be shorter due to thermal sensor fatigue. A new sensor head is rather expensive. Another issue is that the power consumption makes it less suitable for long time test without external power supply.

Measurable gases:

Oxygen

Crystec [31] and Meeco [32].

3.1.7.3.1.3 Pellisters (catalytic)

Working principle:

The catalytic sensor consists of a pair of matched elements usually called detector and compensator. In the detector a platinum wire is embedded in a bead of catalytic material and the compensator have the same design except from that the bead is made of an inert material. Both elements are connected in a Wheatstone bridge circuit. A supply voltage heats the circuit to approximately 500-550°C. This will cause combustible gases to oxidize on the detector and not the compensator with the result that a difference in resistance arises. This produces a measurable output. The compensator also helps compensate for ambient changes in temperature, pressure and humidity which affect both elements equally.

General overview:

This is original method of gas detection that formed the ground for modern technologies. It is a very common method for detecting various kinds of combustible gases. They are relatively cheap but the quality may differ between different suppliers. The response time characteristics are quite poor. The sensor has a lifetime for about two years and is then worn out. The accuracy is generally not sufficient for the type of application intended in this report but have to be further evaluated.

Measurable gases:

Hydrocarbons (C_xH_y),

3.1.7.3.1.4 Metal oxide semiconductor (MOS)

Working principle:

Two electrodes are connected to a film of metal-oxide. The resistance between the electrodes is affected by either an oxidation or a reduction on the semiconducting layer of metal-oxide when it is heated to 250-400° C.

General overview:

This is a highly sensible method capable of detecting toxic gases down to ppb level. The response time is very good, the lifetime is long but the power consumption is high. It suffers from poor selectivity but its cheapness and ease of use have resulted in a rapid development. The problem with the selectivity has not yet been solved but this does not have to be a problem if the environment is controlled.

Measurable gases:

Alcohols, ammonia, butane, carbon monoxide, chlorine, ethylene, heptane, hydrogen, hydrogen sulphide, methane nitrogen dioxide, ozone, propane, sulphur dioxide, toluene, etc.

Nose-network [33], AppliedSensor [34] and Detcon [35].

3.1.7.3.1.5 Paramagnetic

Working principle:

Oxygen is one of few gases that have a strong paramagnetic susceptibility. Paramagnetic susceptibility means that if a magnetic field is present the substance is magnetized parallel to the field and in an extent that is proportional to the strength of the field. This property is used in the sensor. Two spheres filled with an inert gas, usually Nitrogen, is mounted on a suspension that can rotate freely. The arrangement is held within a non-uniform magnetic field. The surrounding oxygen is attracted to stronger side of the magnetic field which results in a force that makes the two spheres rotate. The rotation is fed back via a photo cell to a coil around the rotating assembly. A current is led through the coil to prohibit the rotation. The current needed to accomplish this is direct proportional to the amount of oxygen present.

General overview:

The sensor has very good time response characteristics, no consumable parts are needed and it offers excellent precision over a range from 1-100% oxygen. It suffers from the problem that other gases have small amount of paramagnetic susceptibility which interferes in the measurement if they are present. It is usually no problem because the interference is quite small especially from gases constituent in ambient air.

Measurable gases:

Oxygen

Answers, Paramagnetism [36].

3.1.7.3.1.6 Conducting organic polymers (COP)

Working principle:

A thin polymer film is coated on the sensor structure. Polymers used are for example Polypyrrole and Polyaniline. The polymer is conductive and the resistivity changes when a gas is present and interacts with the polymer matrix.

General overview:

This method is interesting because the sensing material can be built in to an existing construction. They have a high sensitivity, are small and cheap. Problem are poor reproducibility in the fabrication process, they are sensitive to humidity and the drift over time due to oxidation.

Measurable gases:

Adjustable over a wide range.

NOSE-network [33].

3.1.7.3.1.7 Metal Oxide effect transistors (MOSFET)

Working principle:

These types of sensors are usually called GASFETs when they are used to measure gas. An external gate voltage is supplied. When a gas is present the voltage alters. The change of this is measured when trying to keep the current through the transistor constant.

General overview:

This type of sensor is very small, about 1mm^2. They are cheap and have a uniform quality in fabrication. Low sensitivity to moister and stability make them suitable for the type of applications discussed here.

Measurable gases:

Molecules containing Hydrogen and other polar compounds.

NOSE-network [33].

3.1.7.3.1.8 Bulk acoustic wave sensors (BAW)

Working principle:

This sensor is built on the quartz crystal microbalance principle that is covered under the heading “QCM (Quartz crystal microbalance)”.

General overview:

Depending on the coating it is sensitive to different types of gases. This allows it to be tailor made. The detection level is about 10ppm. The sensor is temperature dependent and should be used in room temperature. Advantages are the high stability of the signal and the high reproducibility in production. A disadvantage is the high price.

Measurable gases:

Adjustable over a wide range.

NOSE-network [33].

3.1.7.3.1.9 Surface acoustic wave sensor (SAW)

Working principle:

This sensor is built on the quartz crystal microbalance principle that is covered under the heading “QCM (Quartz crystal microbalance)”.

General overview:

The same characteristics as the BAW apply to this type of sensor. The only difference is that the SAW measures surface acoustic waves which can oscillate with a much higher frequency. Theoretically the SAW would have a higher sensitivity than to the BAW but the noise level also increases with the frequency. However, there are other factors affecting the signal dependency that provides additional information compared to the BAW.

Measurable gases:

Adjustable over a wide range.

NOSE-network [33].

3.1.7.3.2 Gas detection with spectroscopy

The study of matter interacting with electromagnetic radiation is called spectroscopy. There are many different methods used in the field of gas measurements. The principle for conventional laser absorption spectroscopy is that a laser beam is directed through a gas sample and concentration of the gas is calculated from measuring the absorption. This can be done because different gases absorb light at very specific wavelengths. The laser sweeps the specific wavelength very narrowly and the outgoing intensity is measured and correlated to the gas concentration. Fredrik Hansen [37].

Other methods exist though like, Chemiluminescence Spectroscopy, Atomic Emission Spectroscopy, Mass spectroscopy, Photo acoustic spectroscopy, Magneto acoustic Spectroscopy, Tuneable diode laser absorption spectroscopy, etc. Some of these methods are discussed below. This category of measurements usually suffers from high prices on the equipment but much effort is invested in developing portable solutions thus making smaller and cheaper components. If one of these methods is to be used for package integrity testing, a sample must be extracted from the package except from one method that uses the compliment of a fluorescing pad mounted inside the package. There is a possibility that research will lead to the development of a method that has the ability to measure through the walls of a container, even if they are not transparent, but this lies in the future. Rochester Institute of Technology, Spectroscopy [38].

3.1.7.3.2.1 Mass Spectroscopy

Working principle

A gas sample is in the first step ionized. For this purpose there are several different methods. The ions are in vacuum accelerated through a magnetic field. The ions are sorted with respect to the mass-charge ratio. This is achieved by altering the strength of the magnetic field. Only the ions with the desired mass-charge ration will pass the field and collide with a collector. This generates an electric current which is amplified and detected.

General overview

This type of equipment is generally very expensive. It is used in laboratories to analyze molecules but can be used for gas measuring. The accuracy lies below 5ppm which is very good. It’s very flexible and can measure all types of gases. The drawback is that a sample has to be extracted in order to measure.

Measurable gases

A wide range of gases

JEOL [39], University of Illinois, Mass spectrometry [40] and Astbury University, an introduction to Mass Spectrometry [41].

3.1.7.3.2.2 Photo acoustic spectroscopy

Working principle

When exposing a gas sample to infrared modulated radiation this excites the molecules in the sample. When the molecules return to their relaxed state they produce heat which results in sound waves produced as periodic pressure oscillations. By detecting and measuring these waves it is possible to determine the quantity of specific gases in the sample.

General overview

This is a new technology providing high accuracy measurements in real time good portability due to the low power consumption and small size. Wireless communication is already an option, and the price is competitive to other comparable equipment. This is an option for the future when thinking of doing mass-tests on packages. In this case measuring CO_2 is considered.

Measurable gases

Gas/Vapour	Formula	DL, ppm	Gas/Vapour	Formula	DL, ppm
Acetaldehyde	C_2H_4O	0.1	Formaldehyde	CH_2O	0.04
Ammonia	NH_3	0.2	Freon 13	$CCIF_3$	0.04
Carbon dioxide	CO_2	1.5	Methane	CH_4	0.1
Carbon monoxide	CO	0.2	Phenol	C_6H_6O	0.008
Chloroform	$CHCL_3$	0.04	Sulphur dioxide	SO_2	0.3
Diethyl ether	$C_4H_{10}O$	0.02	Toluene	C_7H_8	0.04
Nitrous oxide	N_2O	0.03	Vinyl acetate	$C_4H_6O_2$	0.007

Table 2. Detection limits for gases using PAS system according to Applied nanotech inc [42].

ANI's Photoacoustic platform [42].

3.1.7.3.2.3 Magneto acoustic Spectroscopy

Working principle:

The principle is the same as for a Photo acoustic sensor except from the fact that oxygen does not absorb infrared light. Instead this sensor utilises a pulsating magnetic field to produce the measurable acoustics. When exposed to the magnetic field the gas will start expanding and extracting causing pressure waves. These pressure waves are proportional to the concentration of Oxygen present.

General overview:

The good time response allows real-time measurements. The accuracy is as good as mass spectrometers. Stability means long time between calibrations.

Measurable gases:

Oxygen

Luma Sense, Magneto Acoustic spectroscopy [43].

3.1.7.3.2.4 Oxygen analyse with fluorescing oxygen sensitive film

Working principle:

The system contains oxygen sensitive film, a reader-pen and oxygen analyser equipment. The oxygen-sensitive film is made by a fluorescent dye mixed with a hydrophobic polymer and is placed inside the package in connection with a translucent surface. There is one blue LED-light and one photo detector mounted on the reader-pen. When the film is exposed to blue light, it absorbs the light and emit red light, see Figure 8 for principle sketch. The fluorescent light from the dye is quenched by the presence of oxygen and the lifetime of it is shortened. The characteristic of the fluorescent is detected by the photo detector and transformed to an oxygen-concentration by the analyser equipment.

General overview

The equipment has a detection limit of 300ppm, and an accuracy of 5% of measured value. This equipment could be used combined with a package evacuated from oxygen. When the pad is mounted and the package filled and sealed there is no limit of the number of measurements. Unfortunately the accuracy is not good enough, especially when the concentration level rises, but with future improvement this might become an interesting alternative, especially if other gases can be used.

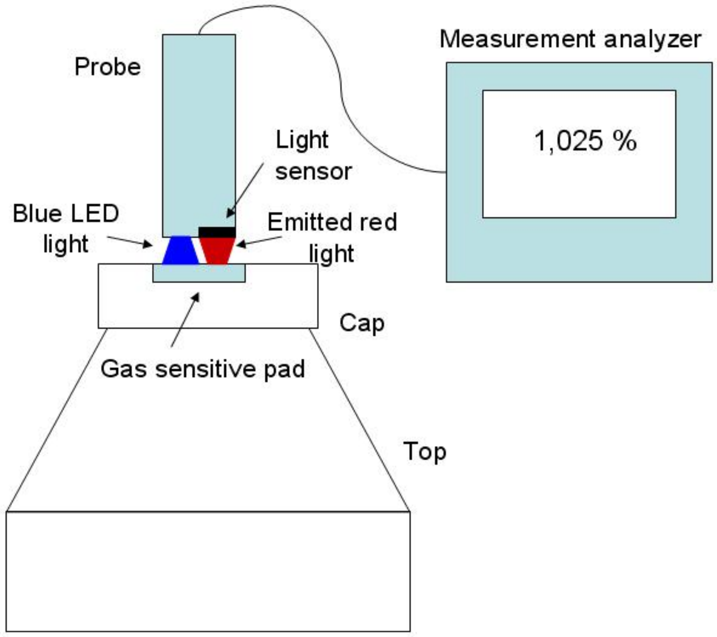


Figure 7 shows the principle of using oxygen sensitive pad for gas analyze.

Measurable gases:

Oxygen

Oxysense [44].

3.1.7.3.2.5 Photo ionisation detectors (PIDs)

Working principle:

A gas is submitted to a beam of ultraviolet light. This creates an ion when an electron is temporarily displaced from the gas molecule. When the molecule reforms with the electron a current is formed. This current is measured and gives a reading of the gas concentration. Gases have different ionization potential which is measured in electron volts. This potential indicates how much energy needed to ionize the gas. The UV lamp emits light energy which also is measured in electron volts. This mean that a PID can measure all gases that have a lower ionization potential than the energy the UV lamp emits.

General overview:

This method can be used to detect many different chemical compounds. It is good for low level detection, down to 5 ppb. New designs have become smaller and cheaper. This type of sensor give a non-specific response which means that they can not distinguish between different gases it responds to. This is no problem because the ionization level of the three largest constituents of ambient air is high enough to not interfere, and the tracer gas is free of choice as long as the PID can sense it.

Measurable gases:

In order of sensitivity: Armatics, Iodine compounds>Olefins, Ketones, Ethers, Amines, Sulphur componds>Esters, Aldehydes, Alcohols, Aliphatics>Chlorinated aliphatics, Ethane>Methane (no response)

Kanazawa University [45] and RAE Systems [46].

3.1.7.3.2.6 Flame ionisation detectors (FIDs)

Working principle:

This sensor type uses the same fundamental principle for measuring gases as PIDs, but instead of ultraviolet lamp it uses a Hydrogen-air flame to ionize the sample gas.

General overview:

FIDs are calibrated to measure other types of gases than PIDs. The measuring range starts at ppm level unlike PIDs that start at ppb level. FIDs are also bigger, heavier and more expensive. One of the few advantages compared to PIDs is a better linearity in the response at higher concentration level (>1000ppm).

Measurable gases:

In order of sensitivity: Aromatics, long-chain compounds>Short-chain compounds (Methane)>Chlorine, Bromine and Iodine compounds.

RAE Systems [47].

3.1.7.4 General references

General references regarding the whole gas chapter;

- MNT, Gas sensor roadmap 3.0 [48]
- ACD, A summary of gas detection [49]
- Systech Instruments [50]
- PTAC, Methods used for air emissions and leak detection and quantification [51]
- Pacific Northwest National Library, Sensor Breakthroughs [52]
- MNT, Gas sensor roadmap 3.1 [53]
- Sensors, Acoustic wave technology sensors [54]
- E2V, Gas sensor technology [55]

3.1.8 Visual surveillance system

A visual surveillance system could use video-cameras to observe any deformations, or leakages on the packages. The system can either be observed by humans, or by advanced software programmed to detect changes in the picture.

3.1.8.1 Heat camera

A heat camera responds to infrared light and visualizes temperature differences in colours. This idea is based on a high resolution heat camera, placed outside the package, monitoring the cap and top carefully. A leakage would lead to a temperature difference between the media leaking out and the stressed plastic surrounding it.

A heat camera found on the market has a temperature resolution of 0.05 °C at 30°C , picture resolution of 640x480 pixels and a updating frequency of 60 Hz. Infrared cameras Inc [56].

3.1.8.2 High-speed camera

Normal video-cameras have a picture update frequency that is to low to detect a temporary leak. With duration of possibly down to 4 ms or even below, finding a temporary leak demands a high-speed camera.

This idea is based on a high-speed camera that monitors the cap and top. An opening is observed by either watching the film or using software to scan the film. Requirements for this method to work are transparent caps and preferably a coloured fluid.

A high-speed camera available on the market can take several thousands of pictures a second, and have mega pixel resolution, Amtele [57].

3.1.9 Pressure solutions

Pressure solutions imply both detecting a decrease of pressure on the tightening surfaces and applying a pressure differential between the inside of the package and the outside environment. It is possible to start without a pressure differential but the idea is to enhance the result by starting with a pressure differential.

3.1.9.1 High pressure

This method is based on applying a high pressure inside the package. A pressure sensor placed inside the package log the pressure. A reference measurement is made before the test. After submitting the package to different load another measurement is made to confirm that no change in pressure has occurred. The measurements have to be made in a controlled environment regarding pressure and temperature.

3.1.9.2 Vacuum

Instead of using high pressure when testing the package, a low pressure or vacuum can be used. This method works similar to the one mentioned above. The degree of vacuum inside the package can be measured in different ways. It can be measured either by a pressure sensor inside the package or by measuring the perimeter. The perimeter can be measured either manually or by a monitoring system. The increase of pressure can be logged. If the pressure does not increase the package is tight.

3.1.9.3 Pressure sensitive film

This idea is based on measuring the pressure between the tightening surfaces. By using a pressure sensitive film a lack of pressure can be detected. If the pressure reaches zero this would imply a possible leak. Different types of sensitive films are available on the market. If the film is exposed to a pressure it changes in colour. The film as a stand alone solution is obviously not applicable to this problem but sensors using a pressure sensitive film can be used. The sensor consists of many piezoresistive sensor elements and has a minimum thickness of 0.3mm. Sensor Products Inc [58].

3.1.10 Electromagnetic radiation

3.1.10.1 Measure of light, Photomultiplier.

This idea is based on the fact that if a leak occurs, light can enter the package. It is possible to measure the intensity of the light with a photomultiplier. See principle below in Figure 9;

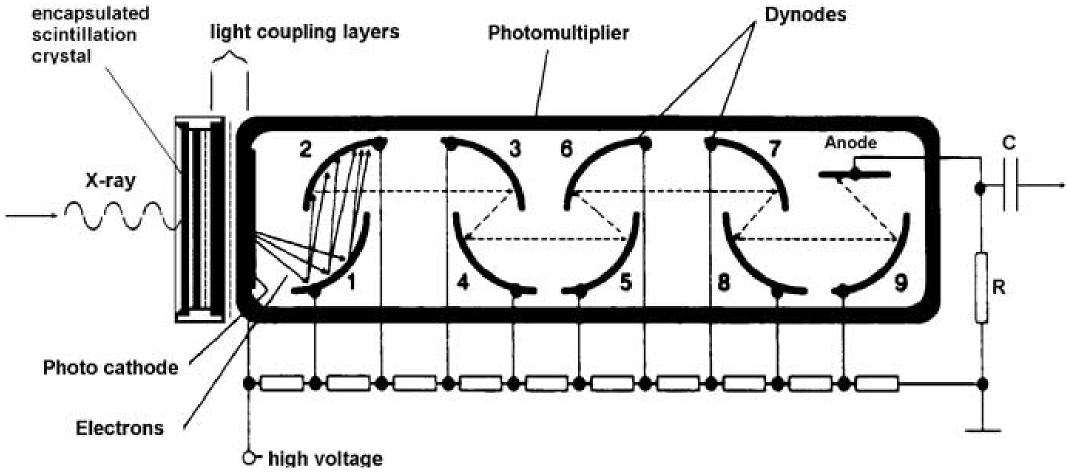


Figure 8 Components of a photomultiplier. Picture is taken from Bruker AXS [59].

A scintillator is a substance that absorb electromagnetic radiation, in this case visible light, and response by fluoresce photons in a longer wavelength. The photons transfer on to a photocathode. A photocathode is a negative charged electrode coated with a photosensitive compound. When a photon hits the photocathode, electrons are emitted due to the photoelectric effect. The electrons are directed with a focusing electrode towards the electron multiplier, consisting of dynodes. At every dynode the electrons are multiplied by the process of secondary emission, commonly five electrons are emitted for every incoming electron. Secondary emission is a phenomenon where additional electrons are emitted from the surface of a material when an electron impacts the material with sufficient energy. All electrons are finally receiving an anode. The arisen current can be measured between the cathode and anode. The photomultiplier can detect single photons and have an amplification of 10^7.

The method is based on mounting a photomultiplier inside a package in order to discover a leak by the incoming light. The realisation of this idea would probably be a laboratory setup, both due to the need of high voltage, minimum>1000V, and that the sensor has glass coating. There are other techniques to measure light in similar way, called avalanche photodiodes. National Encyklopedin [60].

3.1.10.2 Camera-film

This idea is taking use of the photosensitive film used in old cameras. The photosensitive film is a plastic film, coated with small light sensitive grains. The grains are silver-halide crystals held in a chemical suspension. The grains undergo a chemical reaction when the film is exposed to light. The film can be developed using photochemistry.

By placing a piece of a camera film in connection to the tightening area, it could record an opening of the tightening. The package is prepared with film and can be tested without any restrictions. Afterwards the film is developed in a darkroom to reveal traces of a leak. “How Stuff Works” [61] and Våglära och Optik [62].

3.1.10.3 Radioactivity

Radiation appears in different forms. The concept “ionising radiation” contains both electromagnetic radiation and particle radiation. Radiation is emitted from naturally occurring radioactive minerals or artificial materials but can also be created in an X-ray tube by electricity. Ionising radiation contains much more energy than optical radiation. Because ionising radiation causes severe damage to human cells, there are well developed ways of detecting radiation.

This method is based on filling a package with liquid containing radioactive tracers of. The radioactivity outside the package is measured to reveal a leak. The leakage can be traceable with handheld equipment. Radioactivity is used in many applications like flow measurement, humidity measurement, radiography etc. Parts and tools from these might be applicable for this method. Cautious must always be taken when working with radioactivity. Statens Strålskyddsinstitut [63] and Health and Protection Agency UK [64].

3.1.10.4 X-ray

X-ray is commonly used in medical applications but also in food-industry to make sure no stones, glass or other undesired materials have entered a package. X-ray uses electromagnetic radiation created by an X-ray tube. The radiation is only able to travel through certain materials and leaves a spot on the screen where it can not get through.

This method is based on the idea to fill the package with a medium X-rays can not get through. After exposing the package to a load, the tightness area is examined by an X-ray. A leak containing the media would show as a spot outside the tightening.

Mettler Toledo [65].

3.1.10.5 Light detection with small camera

There are small video cameras that are very light sensitive, mostly used by police and military, to look into rooms without detection. The camera lens is connected with fibre-optic to the camera and can be very small. Pär Holman [66].

The idea is based on using a small light sensitive video camera mounted inside the package surveying the tightness area. To improve the possibility of discovering a leakage there must be strong light source outside the package. A benefit of this method is that the position of the leakage can be detected. A robustness test can be performed while the camera monitors the tightness area.

3.1.11 Sound

Sound is mechanical waves that propagate in a matter. Sound travels with different speed through different matter, and is reflected differently at different surfaces.

3.1.11.1 Ultra sound

Ultra sound is sound with a frequency higher than 20kHz. Ultra sound has many commercial applications in medicine and industrial application. The most common are diagnostic sonography, material testing, thickness measurements, cleaning and processing.

This method is based on using ultrasound to find air-pockets or holes. When sending ultra sound through a material irregularity, for example an air-hole, it will be exposed due to the difference in composition, see Figure 10 for principle sketch. A couple of years ago Tetra Pak had a co-operation with the department of "Elektrisk mätteknik" at LTH to investigate the possibilities to use ultrasound to find crack in the material. At that time the project sunk due to the problem not being able to use sufficiently high frequencies, but this constitutes no problem today. Sonotec [67] and PTI [68].

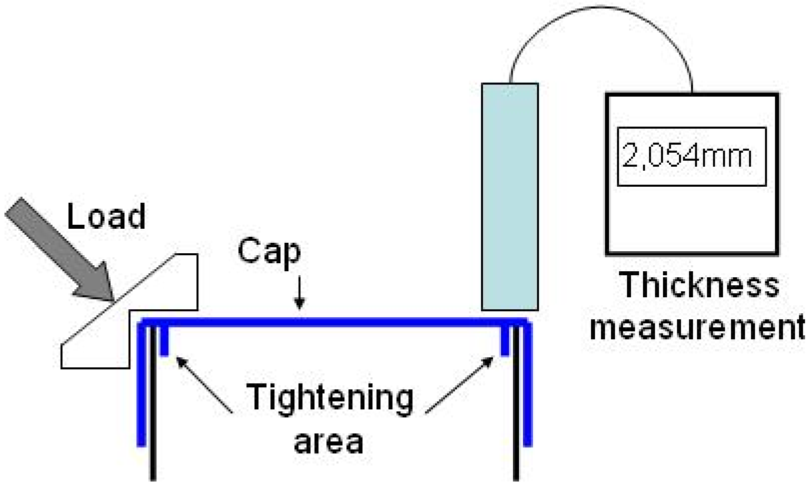


Figure 9 shows the principle of how ultra sound would be used to find air-pockets when a package is exposed to a load.

3.1.11.2 Detection of specific sound

One of the properties of sounds is that it propagates differently depending on the matter. A speaker can be placed on the outside and a microphone inside the package. The speaker sends out a sound wave in a specific frequency which is received by the microphone. If the microphone is equipped with highly accurate filters that sort out all other frequencies, a leak would appear as an increase in amplitude due to air-channel. A benefit with the method is that it measures in real time.

3.1.11.3 Detection of sound from leakage

When leaks occur they are accompanied by a sound that is generated by friction. The sounds lay in the ultrasonic wave frequency and can be detected by ultrasound sensors. The sounds are received and converted in to electrical signals. The fact that other sounds are present is no problem because they differ in frequency form the sound generated by the leak and can be filtered out. This technique is already in use when detecting leaks in pressurised systems. Whether the technique is sufficient for detecting leaks that might be present only for a short time has to be examined. Sonotec [67]

3.1.12 Deformation detection

3.1.12.1 Strain Gauge

A strain is made of a material that changes electrically resistance when being deformed. If a constant current is led through the strain gauge, a deformation causes a change in the voltage due to the different resistance.

The basic idea of this method is that strain gauges are used to sense an opening of the cap. If the stain-gauges are placed around the cap, connected between cap and neck, a deformation in the tightening area can be detected. See Figure 11 for principle sketch. The signal would be transferred out wireless or stored in a memory on the board.

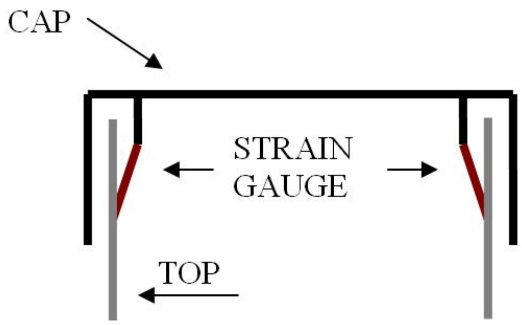


Figure 10 shows how strain gauges would be used to discover an opening of the cap.

3.1.12.2 Strings that brake at deformation

Very thin strings would be mounted inside the ring of the cap, similar to a spider web. If a deformation of the cap would appear, the strings in that area would brake. It would be important that the strings are brittle and does not strengthen the tightening, see picture below.

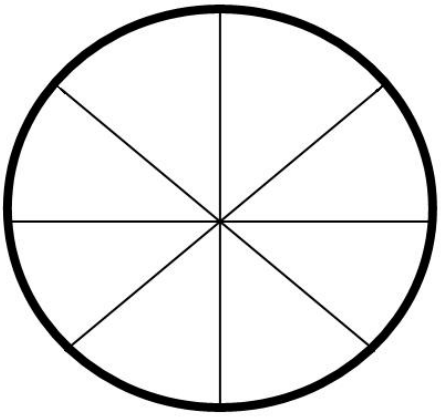


Figure 11 shows the cap seen from under with the breakable strings.

3.1.13 Other ideas

Some of the ideas under this section are ideas that can be combined with others as complements, ideas that could work in the future etc.

3.1.13.1 Modified cap

If the cap was modified, with for example a hole in the centre, a sensor could be mounted in a beneficial way to improve the sensitivity.

By creating a second tightening between the caps lower edge and the top, the space between the threads can be used to keep a reagent or any other usable substance in place. This second tightening can be achieved with tape or preferably a breathing material that is water resistant.

Manufacture the cap and the neck in a material that is plastically deformed in case of a load. This would prevent a temporary leak to close thus making it stationary and easier to detect.

3.1.13.2 Particle movement

This method is based on the idea that smoke inside the package would visualize a leak. The flow can be monitored by a camera or some other kind of equipment that are able to detect the flow a leak would create.

3.1.13.3 QCM (Quartz crystal microbalance)

A QCM is an ultra sensitive mass sensor. It is able to detect mass changes in the nano-gram range. The physical basic is piezoelectricity. In the 1920´s the first quartz crystal controlled oscillator was described. In 1959 the proportional relationship between the oscillation frequency of quarts crystals and added mass was pointed out by Gunter Sauerbrey. The sensors today consists of a piezoelectric quartz crystal placed between to electrodes. When a voltage is applied to the electrodes the quarts crystal starts to oscillate due to piezoelectricity. This oscillation is generally very stable. If a substance is to be detected a rigid layer of it has to be evenly deposited to one or both of the electrodes. This is achieved by coating the surface of the electrodes with a material that attracts the desired substance. The resonance frequency will then decrease according to the Saurebrey equation depending of the mass attached to the electrodes. This method has a detection limit of 10 ppm for gases. The sensors are tailored for their applications and might with research and development be able to detect bacteria or other substances of interest, example of sensor design can be seen in Figure 13. Pharmaceutical international [69] and AppliedSensor Sweden AB [34].

Figure 12 . An example of a QCM sensor, picture is from QCM-sensors [70].

3.1.13.4 Biosensor

A biosensor is a device that consists of a biochemical/biological component mounted in close connection with a signal-transmitter. The principle of the sensor is that the bio-based component reacts with another medium, where one of them is close to the signal-transmitter. The reaction produces a signal, usually electric, which is received by the signal-transmitter. Biosensors are not very established on the market yet but a lot of research is made in this field. A biosensor could be tailored to detect for example bacteria or gas. Thomas Laurell [71], National Encyklopedin [72] and "What are biosensors?" [73].

3.2 Selection process

In order to succeed with the selection process, different criteria must be set up. The criteria includes properties and requirements that weight for or against an idea. All ideas are evaluated against these criteria and a selection is executed. Because the possibility to thoroughly test the methods does not exist, the selection process aims to pick out the best ideas based on the information available.

3.2.1 Criteria

3.2.1.1 Properties of test methods

This section points out the physical properties important to consider when the different methods are evaluated. Each method is judged according to its own abilities depending on what the test is aimed for. In this context the issue is how a certain method fulfils the demands, according to what is necessary, to produce a significant result. The following aspects of the term properties are considered. Not all of them apply to each method.

- Detection level. This is a term describing the smallest quantity possible to measure with a certain method.
- Accuracy. Usually given in the specification sheet of sensors.
- Resolution. Usually given in the specification sheet of sensors.
- Measuring range. If the measuring range is not in the right field or if it is too narrow the method might not be suitable for the application.
- The capacity of the equipment to withstand outer disturbances like temperature, pressure, vibrations and impacts, without deliver invalid results.
- Reproducibility. The possibility of reproducing the results must be fulfilled. Sensors commonly have reproducibility given in the specification sheet. When using bacteria, it must be considered that they are living organisms that can die.
- The period of time the equipment can be functional and deliver valid data without calibration or running out of power.

3.2.1.2 Implementation

To get statistical significance large quantities of test objects must be used. A very important issue is therefore the time consumption of a certain test method. Of course the purpose of the test differs and concern must be taken to whether it is a preliminary test or a full scale test. How easy a method is implemented have a large impact of the choice of method presupposed that the methods can solve the problem. Aspects that affect the implementation are listed below.

- The preparation and performance of the test must not take too long time. Too long time is a diffuse limit and has to be considered more thoroughly when a method is evaluated before an investment. In this case only methods with unreasonably long preparation time are sorted out.
- The preparation and performance of the test must not be too complicated. If the test can not be performed without involving specialists or consultants, the costs and limits of it, must be considered.
- The reading and interpretation of the results should preferably be as uncomplicated as possible. The results must be unambiguous.
- The use of toxic or in any other way hazardous substances should be minimized. The method must be safe for both humans and nature.
- Can a package be tested several times without any risk of jeopardizing the result? If a package can only be measured once, statistics have to be used, which result in extra uncertainties.
- It should preferably be possibility to apply loads without any restrictions.

- Is the method general, or does it only apply to a certain type of package?
- Is it physically possible to implement the method, concerning dimensions or other physical restrictions?

3.2.1.3 Significance of result

Always when measuring there is a risk that measurement it self affect the result. This problem must be minimized and there should be a striving to make realistic tests. Test methods recommended by ASTM or PIRA might not always be applicable to new types of packages. It is important to understand the purpose of a specific test and try to adjust it to current circumstances. In the end the most important issue is the quality of the products that enters the consumers.

Whether a test is performed in a laboratory or in a realistic environment is of no importance for the result as long as it has been established that the method mimics the types of stresses that occurs in a realistic situation. These kinds of adjustments are not always easy to obtain. To keep a safe margin it is better that tests in laboratories exceed the stresses that occurs in realistic environments.

Some methods require preparations that affect the package. It might include being produced with special materials, mounting of sensors, drilled holes in cap or top etc. All these adjustments can affect the result of the test. The influence must be carefully elucidated.

Test methods can be destructive or non-destructive. This thesis is focused on developing a test method for testing packages during development. This allows the test method to be destructive, which means that the package is consumed after it has been tested. There is a possibility that some of the method summoned here can be used as test methods in production.

3.2.2 Coarse selection

In the evaluation process, the above listed criteria have been interpreted according to fit each method. For a coarse selection, different colours are used to indicate how the methods adapt to the problem. The result is shown in Table 3. The purpose is to eliminate methods not suited for the task. The evaluation is based on the problem of temporary leakages. Some methods discarded could though still be useful for detecting permanent leakages.

Colour interpretation;

🟥 Do not fulfil requirements

🟩 Fulfils the requirements

▨ Might fulfil the requirements

🟨 Could be interesting after additional research

🟧 Better methods are available

🟦 No judgement due lack of adequate data or the general structure of the idea

	Criteria		
Measuring method	**Properties of test method**	**Implementation**	**Significance of result**
Bacterial solutions			
Bacteria immersion	🟩	🟥	🟥
Bacteria specific placement	🟩	🟩	▨
Bioaerosols	🟩	▨	▨
Dormant bacteria	🟦	🟥	🟥
Chemical solutions, visual reactions			
Colour indicator	🟦	▨	🟦
Burning	▨	🟧	🟦
Colour indication with enzymes	▨	🟥	🟥
Chemical solutions, measurable reactions			
Citrus acid / pH-reactant	🟧	🟧	🟧
Baking powder/vinegar	🟧	🟥	🟧
Colloids			
Aerosol, solid/gas	🟦	🟨	🟦
Ferrofluid (Magnetic fluid), solid/liquid	🟦	🟨	🟦
Electrical solutions			
Electrical measurement with conducting medium	🟩	🟨	🟦
Electrical conductivity	🟦	🟧	🟧
Footprint			
Coloured liquids	▨	▨	🟥
Scalping	🟦	🟨	🟨
Liquid collector at tightness area	▨	🟥	🟥
Traces from medium	🟦	🟥	🟥
Gas detection			
Sensor mounted inside the package	🟩	▨	🟩
Measure traces of gas in a flow	🟩	🟧	🟩
Extract sample for analyze	🟩	▨	▨
Measuring with radiation	🟨	🟩	🟨
Visual surveillance system			
Heat camera	🟦	▨	🟦
High-speed camera	🟥	🟥	🟥
Pressure solutions			
High pressure	▨	🟧	🟥
Vacuum	▨	🟧	🟥
Pressure sensitive film	🟧	🟥	🟥
Electromagnetic radiation			
Measure of light, Photomultiplier	🟩	🟧	🟥

Camera-film	▨	▨	🟥
Radioactivity	▨	🟥	🟥
X-ray	🟥	🟧	🟥
Light detection with small camera	🟦	🟥	🟥
Sound			
Ultra Sound	🟥	🟧	🟥
Detection of specific sound	🟥	🟧	🟥
Detection of sound from leakage	🟥	🟧	🟥
Deformation detection			
Strain gauge	🟥	🟥	🟥
Strings that brake at deformation	🟥	🟥	🟥
Other ideas			
Modified cap	🟦	🟦	🟦
Particle movement	▨	🟥	🟥
QCM	🟨	▨	🟨
Biosensor	🟨	▨	🟨

Table 3. Result of coarse evaluation of all methods.

3.2.3 Ideas to continue with

Table 3 is the result from the first evaluation of the methods. Motivations of how the colours were chosen are, for each method, explained in Appendix 1. There it is also mentioned if the method can be useful in any other purpose. An explanation of the selection process follows.

Methods with one or more red fields are rejected because they do not solve the problem, or there is some other serious fault that prevents the method to be chosen. A red field is given when own experience or knowledge clearly states the fact that there is no possible way to make an idea work, at least with a reasonable effort.

Ideas with one or more orange fields are also rejected, even if they have green fields, because there are better or easier methods available to solve the task.

Methods with yellow fields are methods that have potential to work if the technology develops within that area. It might also be the case that an effort is needed from Tetra Pak, in the form of evaluation or research, to tailor an idea for a specific setup. These methods are methods that are not ready to be used in the writing moment, but good to keep an eye on in the future.

Blue fields are given methods where it is hard to find information. It can be the general formulation of the idea or because these methods are not used for this purpose that makes a blue field adequate. It might even be case that the method does not even exist. In order to evaluate these methods further research must be done.

A green field is given if it is without doubt or most probable that the tusk is solved by the method. It can of course not be definitely determined before the method is tested and evaluated.

Grey fields are used as a weaker variation of the green fields. It will probably work but there is a little more uncertainty involved.

4 TESTING AND EVALUATION

Tetra Pak is in possession of an oxygen-sensing equipment used to measure the oxygen concentration in the headspace of packages. The equipment had formerly not been used to find leakages. Because the equipment is available and oxygen-sensing is an attractive approach, the equipment was evaluated. The benefit of using oxygen as tracer-gas is that the test can be performed anywhere without restrictions. There is though a problem in reproducing identical oxygen-levels in packages when they are evacuated of oxygen. The highly sensitive equipment demands the initial oxygen-level to be similar in all samples to make the best possible use the resolution.

The basic idea of the method was to extract a sample of the headspace gas-mixture to determine the oxygen concentration. If the initial concentration is known, the measurement shows the difference, which can be caused either by diffusion or a leak. Only one measurement can be made per package, because a measurement is performed by extracting a sample with a needle. To obtain a reference value of the initial oxygen concentration measurements are made on a number of packages directly after the sealing procedure. To evaluate the method, the accuracy and handling procedure of the sensing equipment must be known. It was also of interest to determine whether the procedure used to seal the packages was stable enough to produce a similar oxygen level in the headspace of all packages. Finally the effect of diffusion was tested in order to determine the impact it has on the oxygen level compared to a temporary leak. Tetra Pak had a “Dansensor checkmate 9900” oxygen sensing equipment. For specifications, see data sheet [74]. Tetra Pak also had “dissolved oxygen” measurement equipment available, further on called DO-sensor. These were used together to evaluate the method. A first test aimed to evaluate the Dansensor and to find the smallest, in practice, detectable volume.

4.1 Evaluation-test of oxygen sensing equipment

The Dansensor available at Tetra Pak is an oxygen sensor that measures oxygen concentration in volume percent. According to the specifications it has an accuracy of ±1% of the measured value and a detection limit of 10 ppm. The equipment requires approximately 2ml of gas to be extracted from the headspace to complete the measurement. This is accomplished by inserting a needle through a septum into the package. The needle is connected to the main equipment by a tube.

4.1.1 Goal

This test aimed to find the smallest, for the Dansensor, detectable volume air injected in a container. The injected air contained 21% oxygen and the container held a constant volume where most of the oxygen formerly was removed. When a threshold volume of detectable air was established a theoretical study was done. The purpose was to show how different configurations of pressure differentials and leak sizes affect the time it takes for a flow to add up to the threshold volume. The time-span shows whether it is reasonable to believe that the equipment can be used to detect temporary leaks. In this study a constant laminar flow through a round hole was presumed. The outcome is presented under the heading “4.1.3 Calculations”.

4.1.2 Theory

All involved gases can be assumed to be ideal under the current circumstances, thus the general ideal gas law is applicable. It states

$$PV = mMR_iT \tag{1}$$

where P is the absolute pressure(Pa), V is volume(m^3), m is mass(kg), R_i is the individual gas constant(J/kg K), T is absolute temperature(K) and M is the molecular mass(kg/mol). All units are the same when the variables are used later in the text. Pneumatic flow of gases through leaks can take five shapes; turbulent, laminar, molecular, transitional and choked flow. The type of flow that will appear is influenced by five factors.

- The molecular mass of the gas
- The viscosity of the gas
- The pressure difference causing the flow
- The absolute pressure in the system
- The length and cross section of the leak path

The first four factors can either be controlled or estimated but the geometry of the leak path is at the moment unknown. In this analysis a straight cylindrical hole with variable length and diameter is presumed. Also the entrance condition in the leak, the shape of the flow and the surface finish has an influence on the flow. This is reflected in the Reynolds number. Reynolds number is a dimensionless number which is used in the study of viscous flow through pipes.

In leak testing the most common types of flow are laminar and molecular. Laminar flow is together with turbulent flow one of the two constituents of viscous flow. The first objective is to distinguish between molecular and viscous flow. This is done by calculating the ratio between the mean free path length (mfpl) and the diameter of the leak. The mfpl is the average length a molecule travels before it collides with another molecule. The mfpl can be calculated from equation;

$$\lambda = 116.4\frac{\mu}{\mathrm{P}}\sqrt{\frac{T}{M*10^3}} \tag{2}$$

where μ is the gas dynamic viscosity(Pa*s), P absolute pressure, T absolute temperature, M molecular mass and λ the mfpl(m). In this setup the mfpl can be calculated and the diameter of the leak is varied. If the ratio between mfpl and the diameter is less than 0.01 the gas flow is viscous. When the ratio is between 0.01 and 1 the flow is transitional and above 1 the flow is molecular. Transitional flow occurs in the gradual transition from laminar to molecular flow. If the flow is viscous, the next step is to establish whether the flow is turbulent or laminar. This is done by calculating the Reynolds number for ideal gases;

$$\mathrm{Re} = \frac{\rho v D}{\mu} = \frac{\rho\left(\frac{Q}{A}\right)D}{\mu} = \frac{4\rho Q}{\pi\mu D} \tag{3}$$

where v is the velocity of the gas (m/s), A is the area of the leak (m^2), Q is the volume flow (m^3/s), D is the leak diameter(m), ρ is the density (kg/m^3), μ is the dynamic viscosity. The leakage rate Q is found from Poiseuilles law for viscous volume flow through a cylindrical tube.

$$Q = \frac{\pi r^4}{8\mu l}\left(P_1 - P_2\right) \qquad (4)$$

where Q is the gas volume flow, r is the radios of the leak, μ is the dynamic viscosity, l is the length(m) of the leak, P_1 is the upstream gas pressure and P_2 is the downstream gas pressure. The critical value of the Reynolds number, where the flow transforms from laminar to turbulent flow, is approximately 2100 for smooth tubes with well rounded entrances. The time it takes a leakage to add up to the threshold volume can be calculated by;

$$Time = \frac{V}{Q}$$

Where V is the threshold volume and Q is the gas flow in the leakage. These equations are also used to calculate backwards to answer the question "If the leakage-time and detectable volume are known, what will the diameter of the hole be?".

With the flow for different leaks calculated and the duration-time for a temporary leak known a control calculation can be performed to estimate if there is a chance for a bacterium to pass by the tightening. This is done by calculating the velocity of the gas flow and multiply it with the time of the leakage, which results in the furthest theoretical length a bacterium can travel. If the length is smaller than the tightening the bacterium does not have time to get through. The bacterium can still get stuck in the tightening and continue its travel at another leak, but this requires the leaks to appear with a short time interval so that the bacterium does not die.

Nondestructive testing Handbook [25] and Thermodynamics [75].

4.1.3 Calculations

The gas involved in this test is ambient air.

Air properties

Molecular mass:	0.029 kg/mol
Dynamic viscosity at 20°C:	18 μPa*s
Density at 100kPa:	1.21 kg/m^3

Values for calculations

Universal gas constant	8.315 J/ mol K
d	2, 7 & 10 μm
l	1 & 3 mm
Time of leakage, t	4 ms
Temperature, T	293.15°K
P_{in}	65 - 100kPa
P_{out}	100 kPa

Because air that leaks into the package was of interest, the mfpl is calculated for the air pressure outside the package.

$$\lambda = 116.4\frac{\mu}{\mathrm{P}}\sqrt{\frac{T}{M*10^3}} = 116.4*\frac{18*10^{-6}}{100*10^3}\sqrt{\frac{293.15}{0.029*10^3}} = 6.66*10^{-8}\,m$$

The ratio between the mfpl and hole-diameter determine what sort of flow that will exist in the leak, and is thereby calculated for different diameters.

$$R = \frac{\lambda}{d} = \begin{bmatrix} d = 2\mu m \\ d = 7\mu m \\ d = 10\mu m \end{bmatrix} = \begin{matrix} R_1 = 0.0333 \\ R_2 = 0.0095 \\ R_3 = 0.0066 \end{matrix}$$

From the calculations above it can be seen that for the leak-diameter 2µm the flow is transitional because the ratio is higher than 0.01, but for diameters above 7µm the flow is viscous because the ratio is below 0.01. Calculations are performed for viscous flow due to the small difference.

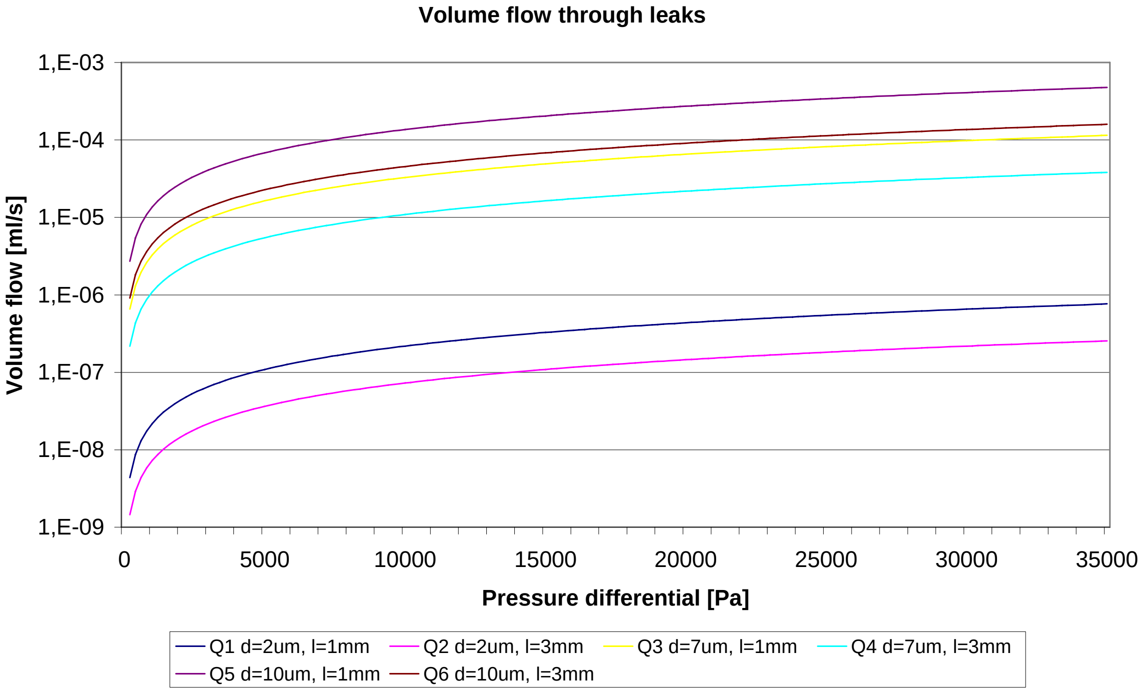


Figure 13 shows how the volume flow changes with pressure differential for different leak diameters and lengths. Negative pressure differential is not concerned because then the leakage is out from the package. Notice the use of logarithmic scale.

Figure 14 shows the result of the calculations of the volume flow in a leak with variation of pressure. A control calculation of the flows characteristics was made by calculating the Reynolds number with equation (3), see Figure 15.

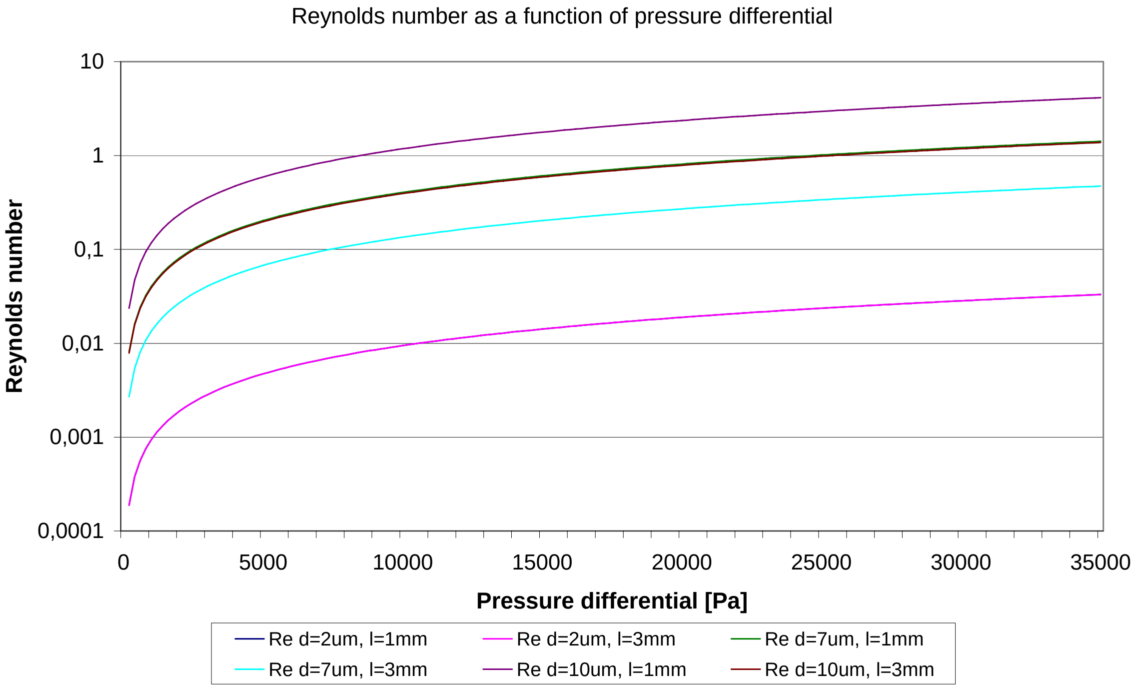


Figure 14. Reynolds number as a function of differential pressure with different leak diameters and lengths. The critical limit for turbulent flow is approximately 2100. Notice the use of logarithmic scale.

The critical Reynolds number for turbulent flow is approximately 2100, which confirm the flow to be laminar.

A control calculation of the maximum travel path for a bacterium. S is the travel path in meters, v is the velocity of the gas, t is the duration time of the leakage and Q is the volume flow of the leakage, the result of the calculation can be seen in Table 4.

$$S = v * t = \frac{Q}{A} * t$$

$\frac{S}{l} > 1 \rightarrow$ Bacterium can get inside the package

$\frac{S}{l} < 1 \rightarrow$ Bacterium stay outside or get stuck in the tightening area.

$\Delta P = 35 \mathrm{kPa}$

d [m]	l [m]	Q [m3/s]	A [m2]	S [m]	S/l
$2*10^{-6}$	$1*10^{-3}$	$7,64*10^{-13}$	$3,14*10^{-12}$	$0,97*10^{-3}$	**0,97**
$7*10^{-6}$	$1*10^{-3}$	$1,15*10^{-10}$	$38*10^{-12}$	$11,9*10^{-3}$	**11,91**
$10*10^{-6}$	$1*10^{-3}$	$4,77*10^{-10}$	$78*10^{-12}$	$24,3*10^{-3}$	**24,31**
$2*10^{-6}$	$3*10^{-3}$	$2,55*10^{-13}$	$3,14*10^{-12}$	$0,32*10^{-3}$	**0,11**
$7*10^{-6}$	$3*10^{-3}$	$3,82*10^{-11}$	$38.5*10^{-12}$	$3,97*10^{-3}$	**1,32**
$10*10^{-6}$	$3*10^{-3}$	$1,59*10^{-10}$	$78,5*10^{-12}$	$8,10*10^{-3}$	**2,70**

Table 4. Calculation of maximum travel path for bacterium. For leaks with diameters of 2µm or smaller the bacterium do not have the time to get inside the package when the leakage time is 4ms. No acceleration time is included in these calculations.

For temporary leaks where the duration time is longer than 4ms it is much more likely for the bacterium to get inside.

Nondestructive testing Handbook [25] and Thermodynamics [75].

4.1.4 Material

The material used in this test can be seen below;

- Container composed by two similar parts manufactured in a 3d printer with constant volume of approximately 100ml. See sketch in Figure 16.
- Injection needle with graded container, one up to 1ml and one up to 500 µl.
- Dansensor checkmate 9900, oxygen sensor.
- Nitrogen flushing equipment; gas-tube, regulator, hoses, check valves and a T-nozzle.
- Septum

4.1.5 Experimental setup

The tests was performed in atmospheric pressure 101.3 kPa and room temperature 23°C 50%RH. The essence of the main test was to inject a small amount of oxygen in a oxygen-free container to see where the practical detection limit was. In order to achieve this, several pre-tests needed to be performed to develop a test method that was reliable.

4.1.5.1 Disposition

The container was equipped with four holes. There were check valves for Nitrogen entrance and exit mounted in two of them. The other two were small (Ø1mm) holes covered with septum, in order to make it possible to penetrate the container wall with injection needles without any gas leaking in or out. One of the small holes was used by the Dansensor when extracting a sample and the other was used for inserting small controlled amounts of air.

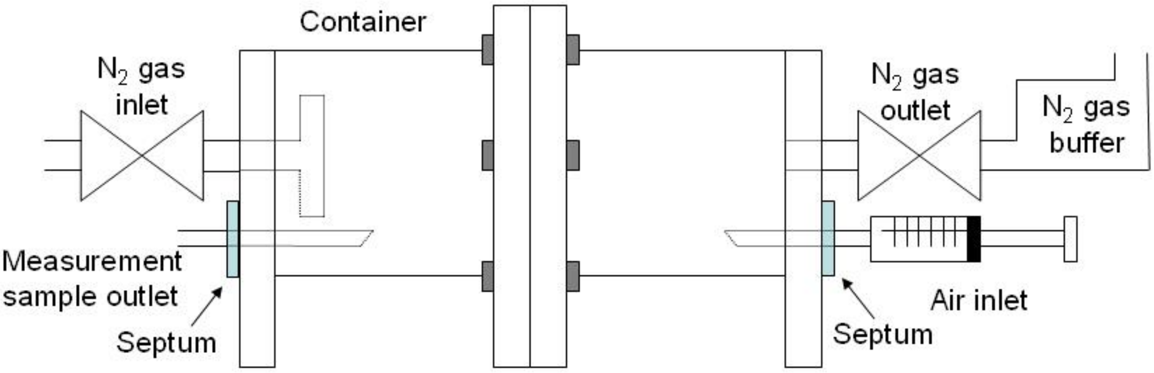


Figure 15. Sketch showing the principle of the laboratory experiment set up.

The T-valve on the sketch had the function of spreading the flow of N_2 to increase the efficiency of the flush, limit the use of N_2 and decrease the flush time. The check valves used for this test had the function of manual closure by tightening a screw. Between the two parts of the container there was an O-ring to keep the container air-tight. There were also O-rings between the check-valves and the container.

4.1.5.2 Test; flushing time

To keep the conditions as similar as possible for every measurement, the flushing should be performed in a similar way every time. The container was flushed for some time, to find a value that was reachable after an adequate time. When a presumably good value was found it was used as initial value for all future tests. The test was performed by flushing the container for a certain time and then one measurement was taken. This was repeated until a steady state was found.

4.1.5.3 Test; container volume

To determine the exact volume of the container, it was placed on an accurate scale. The scale was set to zero when the dry container was placed and standing steady. It was then filled with room-temperate water and the weight was recorded. With the density of room-temperate water the volume was calculated.

4.1.5.4 Test; affect from sample

The goal of this test was to determine if a sample affect the test equipment, the environment or the result in any way. Because the Dansensor extract a sample of approximately 2 ml, out of 100ml, the pressure will be lower than atmospheric pressure. How much lower the pressure will be can be calculated theoretically;

Assumed; temperature, volume and gas-constant are constant. Ideal homogenous gas-mixture.

Ideal gas law, equation (1), PV=mMR$_i$T

$$\text{Constant volume} \rightarrow \frac{m_1 R_i M T}{P_1} = \frac{m_2 R_i M T}{P_2} \rightarrow P_2 = \frac{m_2}{m_1} P_1$$

$$\Delta P = P_2 - P_1 = \frac{m_2}{m_1} P_1 - P_1 = \left(\frac{m_2}{m_1} - 1 \right) P_1 \rightarrow \begin{bmatrix} m_1 = 1 \\ m_2 = 0.98 \\ P_1 = 101.3 kPa \end{bmatrix} \rightarrow \Delta P = -2026 Pa$$

For every sample the pressure decrease with approximately 2%, dependent on the exact sample volume, container volume, initial pressure etc. To see if this decrease of pressure had any affect on the measurement result, a predictive test was performed.

The test was based on comparing results from samples when volume versus pressure has been held constant. The volume was held constant by closing the container when measuring, and the pressure was held constant by opening a buffer containing nitrogen. When performing a measurement the extracted volume will be exchanged with nitrogen from the buffer. Before every test-sequence a flush with Nitrogen gas was performed. This was done to empty the container of air containing undesired oxygen.

Two tests were originally planed. In the first test the container was flushed and then one measurement was made every minute for three minutes. This was done ten times with the container open, constant pressure, 20 seconds flush with 20l/min of N_2.

The second test was performed in a similar manner, but with the container closed after the flush. This test was only performed five times due to spread in result. The cause of the spread had to be found, and therefore more tests were performed. The container was sealed with silicon-grease to prevent any leakages.

Due to suspicion that a high value measurement affects the next coming measurement a third test was performed. The purpose of the test was to evaluate whether measurements were affected by each other, and if so, to find the cause. The test was performed by emptying the container, make one measure outside the container in ambient air, insert the measuring needle and perform three measurements in a row. The procedure was done once every minute for two minutes and the test was performed five times.

To minimize sources of leakage at the check valves, they were changed to bended pipes. These had less components and gaskets. A fourth test was performed by emptying the container and carry out one measurement every minute for three minutes with a constant volume. The volume was held constant by closing the gas inlet hose with the regulator and closing the gas outlet with pliers.

To further minimize sources of leakages, the bended pipes were changed to straight pipes, which had no other tightening than to the container and the hose. A fifth test, similar to the previous was performed, with no satisfying result and the Dansensor was left for calibration and a newly calibrated Dansensor was received. All tests continue with the newly calibrated Dansensor. A sixth test was performed as previous ones but with the pipes exchanged back to check valves.

4.1.5.5 Test; smallest detectable volume

The goal of this test was to determine the smallest detectable volume of air in a chamber of approximately 100ml with the Dansensor 9900. The threshold volume is used as a reference volume in calculations shown before. The calculated values can then be used to conclude whether the equipment and method could work on packages.

The container was first emptied of air, which was achieved with a flush. To establish the present oxygen concentration after the flush a reference measurement was performed before the "real" measurement. The result from the last test showed that a closed volume, with a quick pressure-equalization works best for this test. When a reference measurement has been performed, ambient air was injected. After waiting a fixed time, to allow the oxygen in the injected air to diffuse evenly in the volume, a second measurement was performed.

The test was performed in series of ten measurements with decreasing amount of injected air for every set, in order to reach the desired statistical significance. The start volume was 1ml, and the test volume was decreased with 0.1ml, until 0.1ml was reached, then series with 0.05, 0.02, 0.01 and 0 ml injected air was performed.

A waiting time, long enough for the air to stabilize, was determined before the test could start. By performing tests with 1ml injected air and using different waiting times a proper waiting time was found. Due to a big spread in result and noticing that the Dansensor counts its value downwards before showing a result, search for leaks was performed. This was carried out by filling the container with hydrogen gas mixture and sniffing outside with a hydrogen sniffer, Sensistor H2000plus [76]. No leaks were found on the container. The regulator was examined next. A hose from the regulator was held under water when the regulator was closed. A small gas flow still came from the hose which indicated that the hose was not tight. Therefore an extra check valve was mounted outside the container to enable an easier manual closure of the gas inflow. With this setup new tests were performed. After adjustments from fault-searches the final test procedure for every measurement was;

1. Flush the container with both check valves open until 10ppm concentration was achieved.
2. Close check valve for N_2 inlet.
3. Close outlet hose with pliers.
4. Slowly inject air with syringe.
5. Shortly release closure with pliers to pressure-equalize.

6. Close outlet check valve.
7. Wait for two minutes before measuring.

Measuring needle was held inside the container through all tests.

4.2 Test to investigate influence by diffusion

4.2.1 Goal

The goal of this test was to determine whether the diffusion-rate from outside a package, could be so high that it will not be possible to distinguish between a leakage and diffusion. This is a risk when using a method that does not surveillance the package in real time. The basic idea was to fill packages with de-aerated water with low dissolved oxygen level and evacuate the headspace from all oxygen. When this was done the packages were sealed and stored for varying times in order to have the oxygen concentration inside the packages logged over time.

4.2.2 Theory

Diffusion of oxygen appears both between the water and gas inside the package, but also through the package walls to both headspace and liquid. In practise it is not possible to completely remove the oxygen from neither the headspace nor the liquid. When the result is achieved, it is of interest to know if an increase in the headspace is caused by diffusion from outside the package or from the liquid inside the package. The diffusion from outside to inside the package was, in this case, impossible to calculate due to all uncertainties concerning handmade folding, handmade sealing, tightening, material properties etc. The diffusion between the gas and the liquid inside the package can be estimated by calculations.

4.2.3 Calculations

The purpose of these calculations is to evaluate whether the oxygen transfers from the liquid to the headspace or vice versa after sealing the package. It was possible to measure the oxygen concentration in both the gas and the liquid inside the package. Henrys law can be used with a measured value of oxygen concentration to calculate what oxygen concentration this would result in on the other side from diffusion. By comparing calculated values with measured values the direction of diffusion can be found. Henrys law;

$$y_{i,liquid-side} = \frac{P_{i,gas-side}}{H} \qquad (5)$$

Where y_i is the concentration solute in the solution, P_i is the partial pressure (bar) of the solute above the solution and H is Henrys constant (bar), see Table 5. Henry's law is only valid for dilute gas-liquid solutions and where the solvents do not react with each other. It is also only valid for the surface layer of the solution, but can after a longer time and for smaller volumes of solution be assumed to be valid for the whole solution.

Solute\ Temperature	290 K	300 K	310 K	320 K	330 K	340 K
O_2	38 000	45 000	52 000	57 000	61 000	65 000

Table 5. Henrys constant (bar) in aqueous solutions for different temperatures, from Thermodynamics [75].

At first the concentration of oxygen in water can be calculated from a measured value of oxygen concentration in the gas. With the knowledge of the air-pressure and a measured value of the oxygen concentration in the headspace, the oxygen pressure can be calculated.

$$P_{O_2} = C_{O_2} * P_{air}$$

Henrys constant can be estimated with linear interpolation from Table 4 with a known temperature.

With the knowledge of the oxygen pressure in the headspace and Henry's constant, the concentration of oxygen in water can be calculated.

$$y_{O_2,H_2O} = \frac{P_{O_2}}{H}$$

The DO-sensor is measuring in mg/L, therefore it is convenient to recalculate the concentration to the similar unit. The amount of mole water in one litre of water, called N_{H2O} [mole/L], is calculated by dividing the density of water with the atomic weight of water. The concentration value is then used to calculate the amount of mole/L DO in one litre of water, called N_{O2} [mole/L]. The concentration in [mg/L] is then calculated by multiplying the amount of mole/L DO with the atomic weight for oxygen.

$$N_{H_2O} = \frac{\rho_{H_2O@T}}{10^3 * M_{H_2O}} = \frac{\rho_{H_2O@T}}{10^3 * (2 * M_H + M_O)}$$

$$N_{O_2} = y_{O_2,H_2O} * N_{H_2O}$$

$$C_{m,O_2} = \left(N_{O_2} * M_{O_2}\right) * 10^6$$

The value $C_{m,O2}$ can be compared to a measured value of the oxygen concentration in the water to see in what direction the diffusion-rate is.

A measured value of DO concentration in the water can be used to calculate what concentration of oxygen in the gas this would result in, assuming the gas not to contain any oxygen initially. This is calculated by divide the measured DO value with the atomic weight of oxygen to get the amount of mole DO in one litre of water, N_{O2} [mole/L]. By dividing this value with the amount of mole water in one litre of water the concentration oxygen in the water is received. This value can together with Henry's constant be used to calculate the partial pressure oxygen in the gas above, which divided with the total pressure air gives the concentration of oxygen in the air.

$$N_{O_2} = \frac{10^6 * C_{m,O_2,measured}}{M_{O2}}$$

$$y_{O_2,H_2O} = \frac{N_{O_2}}{N_{H_2O}}$$

$$P_{O_2} = y_{O_2,H_2O} * H$$

$$C_{O_2} = \frac{P_{O_2}}{P_{air}}$$

Equations used in calculations can be found in Thermodynamics [75].

4.2.4 *Material*

- Packages, not sealed.
- Sealing rig. Special made equipment that Tetra Pak uses for sealing prototype packages.
- Nitrogen gas bottle, regulator, hoses and equipment for nozzles.
- WTW CellOx 325, dissolved oxygen sensor.
- Dansensor Checkmate 9900, oxygen sensor.

4.2.5 *Experimental setup*

In order to perform a test to investigate the influence of diffusion, some preceding tests where done. The first part of the tests was to prepare packages and investigate if a steady initial oxygen concentration could be attained. Because the Dansensor is more accurate on low concentrations, a low initial concentration level should be strived for. The packages used for this test were filled from the bottom. They were filled with de-aerated water and then nitrogen was used to evacuate oxygen from the head-space. This procedure was needed in order to get a low initial oxygen concentration before the packages were sealed in the bottom. It was important that all packages were filled in a similar manner to receive a steady initial concentration level.

The bottoms were sealed by inductance sealing, which was completed within a second, in the sealing equipment. The sealing rig was not designed to have any equipment held inside the package while using it, therefore the accessible space was very limited and only a thin crack of the bottom was available. The equipment for rejecting oxygen in the package must be held inside the package while the package was set in the rig. This results in that the equipment for rejecting the oxygen must be thin enough to get inside the crack without harming the package or the rig. Figure 17 shows how the bottom of the package is hoist up.

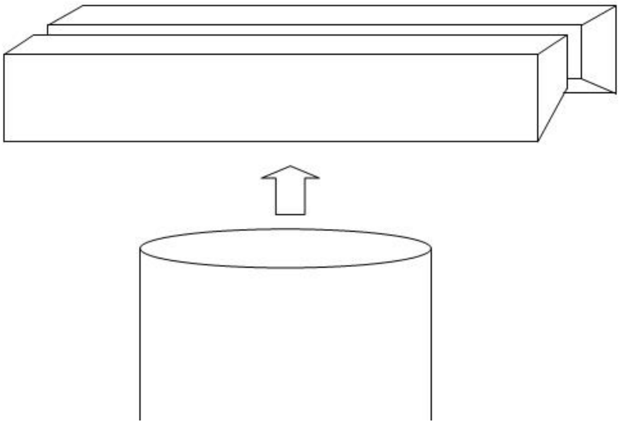


Figure 16 shows how the package was hoist up to the sealing device in the rig. The inside of the package could only be reached through the thin hole above the sealing device.

4.2.5.1 Initial test to fill and seal packages

To investigate the possibilities to de-aerate and seal the packages with the sealing rig, an initial test was performed. For this test the water was not prepared in any way, and the headspace was emptied of oxygen only by blowing nitrogen through the water inside the package. The nozzle used for this test was a special made fork-like tool with three exhausts. It was made by cupper-pipes that were welded together and the pipes to the packages were flattened in order to fit into the thin crack, see Figure 18. After nitrogen has blown through the water long enough, the nozzles were pulled up and the package sealed.

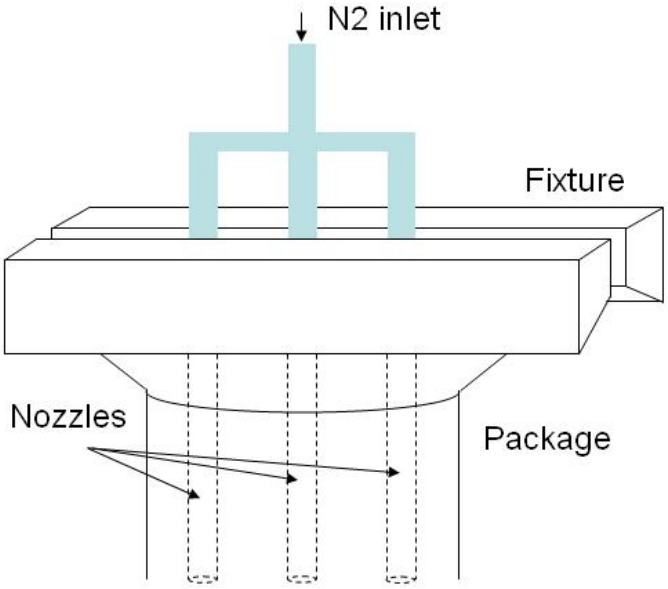


Figure 17. Package fixed in the sealing rig while evacuating oxygen.

After pulling the nozzles up and before sealing the package, the bottom was opened and exposed to the ambient air. This time was critical and of course aimed to be as short as possible, but could create variations in the result. To minimize the risk, a plastic bag was held around the rig to reduce the oxygen concentration in the air around the opening. The plastic bag also decrease risks of getting a nitrogen-flush to the user's face, which in worst case could cause suffocation. This risk was though very small due to the small amount of nitrogen used and the large volume air in the lab.

A first test was performed by mounting the package, with one litre of water, in the rig upside down. The nozzle-tool was then put through the fixture into the package. The package was hoist by the rig into the fixture. While the rig hoists the package, the edges of the bottom were folded correctly in order to fit in the rig. When the package was in place the gas was turned on with various flows and for various times. After some time the nozzle-tool was pulled up and the package sealed. The gas was turned of first when the nozzle-tool was above the package. After the package was sealed it was folded in the bottom, turned upright, and a measurement was done by using a septum and measure at the headspace area. To keep the Dansensor working it was important that the measuring needle was not kept in water.

A final test was performed to see how long time it takes to empty a package with, respectively without any water inside. This was done by measuring the oxygen level continuously at the open bottom while flushing it. The water was not prepared in any way for this test either.

4.2.5.2 Test to empty water from dissolved oxygen

Evacuating the headspace and the water from oxygen was the procedure that was most time-consuming. Because there was only one sealing rig, everything that could be done aside minimize the time for the test. The water could be de-aerated in advance, and was not necessary to be done in the rig. To find the most efficient way of evacuating dissolved oxygen from water, a small test was done. The first part of the test compares water pored up with different temperature, boiled water, and water that were blown with nitrogen. The dissolved oxygen level was measured with a DO sensor.

The second part of the test was based on the result from the first part and different nozzle types were compared to find an efficient method. The nozzles that were tried were based on a cupper pipe with different exhausts. First a normal pipe was used, next a fine meshed net was mounted on the ending with the aim to create smaller sized bubbles. Smaller bubbles result in a larger nitrogen surface towards the water. At last a plastic hose with small holes was mounted on the end of the pipe, see Figure 19. The dissolved oxygen level was measured with five minutes in between.

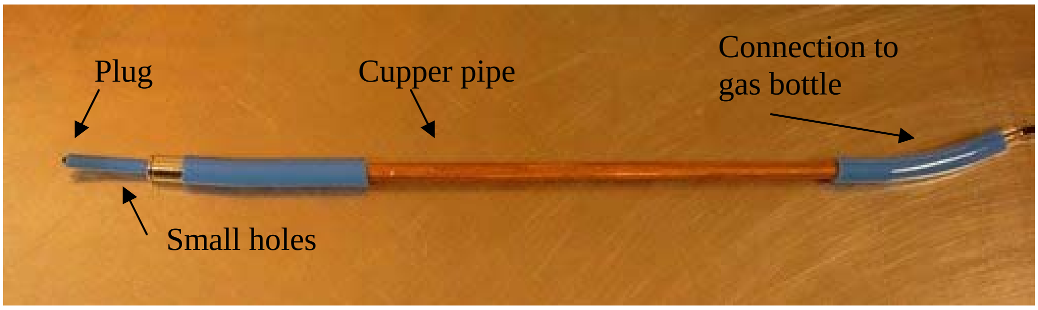


Figure 18. Last version of the nozzle-design consisting of a plastic hose with many small holes.

This test was performed with eight pipes simultaneously which can be seen in Figure 20.

Figure 19 shows the set up when eight packages had their dissolved oxygen removed.

4.2.5.3 Test to determine affect from diffusion

For the first test a plastic bag was used to keep the environment steady above the package. This was difficult to work with and something more rigid was needed. Therefore a hard plastic cover was build. Two extra hoses were mounted on the cover to enable the environment above the packages to be flushed. The cover also had the nozzle-tool mounted fixed inside. The cover is shown in Figure 21.

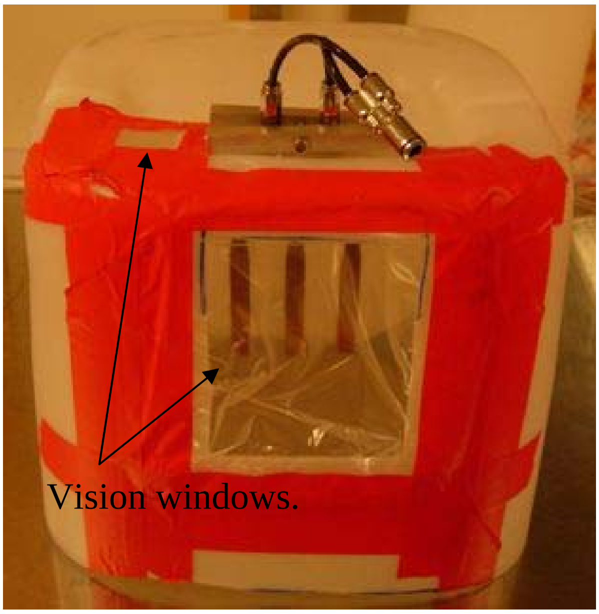


Figure 20. Cover used to keep the environment above the package steady and to keep the oxygen concentration low. Two extra hoses were originally mounted on the top to enable a flush of the environment inside.

The test started with trying out the new cover. Packages was filled with de-aerated water and set up in the sealing rig. The oxygen in the headspace was evacuated. Different waiting times, flows and configurations of gas flow was tried in order to find a method that gave a low and steady initial oxygen concentration value.

The procedure that was worked out for the filling and sealing process was;

1. Fill package with 900gr tap-water, approximately 20-25 °C.
2. Expose water to nitrogen-flow with special made nozzle.
3. Measure DO-level with DO sensor, top limit 0.7 mg/L DO in water.
4. Mount package at sealing-rig.
5. Put cover on top of rig, so that nozzle-tool goes through the fixture.
6. Hoist package while directing edges to the fixture.
7. Turn gas flow on, 30L/min, only into the headspace volume.
8. Start timer, wait for 2 minutes.
9. Turn gas flow off.
10. Pull the cover up and immediately seal the package.

When all packages were filled and sealed they were stored according to Table 5 in a temperate room keeping temperature 23°C and 50% humidity in accordance with ASTM standard [77]. The first five were used as reference packages and were measured instantly after the sealing. The last series were exposed to a vibration test for 30 minutes according to ASTM with assurance level II.

All packages were tested after a slow stir, to spread any oxygen inside the package evenly. The oxygen concentration inside the headspace was measured first, septum was used. When the value was received, the top was cut of and the DO-level was measured with the DO sensor. There were 35 packages tested in total according to the table below;

Time [days]	*Packages*
0	5
½	5
3 ½	5
6½	5
9½	5
13½	5
13½*	5

Table 6 shows the time schedule for the test performance of the diffusion test. (*)The last series was exposed to a vibration test for 30 minutes.

The tests were performed more often in the early stage because then the concentration gradient was higher, which should result in a larger effect.

5 RESULT

Results from the different tests are gathered with small explanations. The results are further discussed under the heading "Discussion/Conclusions".

5.1 Result from oxygen sensing equipment evaluation test

5.1.1 Result of flushing time test

Initial value	14.6%
1 minute	0.006%
1 minute 20 seconds	0.004%
1 minute 40 seconds	0.003%
2 minutes	0.003%

Table 7 shows how the oxygen level in the container decreases the first two minutes when flushing it with nitrogen.

The time it takes to reach a certain value depends greatly on the initial value. It was possible to reach 0.001%, which is the Dansensor detection limit, within an acceptable time range, and therefore 0.001% was set to a start value for the test to find the smallest detectable volume. The time range was about 2-5 minutes for container filled with air, and approximately 30 seconds when the container had a low initial concentration. Table 7 indicates how the oxygen level decrease with time.

5.1.2 Result of test to determine container volume

The measured weight of the water filled in to the container and calculations can be seen below.

Weight of water; 101.3g

Density of water at 20°C; 998kg/m^3

Volume; $V = \frac{m}{\rho} = \frac{0.1013}{998} = 1.015 * 10^{-4} m^3 = 101.5 ml$

5.1.3 Result of test to determine affect of sample

The first test was performed with constant pressure, 20 second flush with 20L/min. New measurements were performed with one minute in between for 3 minutes, see Table 8 for result.

	Sample									
Time [min]	**1 [%]**	**2 [%]**	**3 [%]**	**4 [%]**	**5 [%]**	**6 [%]**	**7 [%]**	**8 [%]**	**9 [%]**	**10 [%]**
0	0.002	0.002	0.002	0.001	0.001	0.001	0.001	0.001	0.001	0.001
1	0.003	0.004	0.003	0.002	0.002	0.002	0.002	0.002	0.002	0.002
2	0.003	0.006	0.003	0.002	0.003	0.002	0.002	0.002	0.002	0.002
3	0.003	0.006	0.004	0.003	0.003	0.002	0.002	0.002	0.002	0.002

Table 8. Result from the first test, with constant pressure, to determine the affects of measuring.

The second test was performed with a constant volume, 20 second flush with 20 L/min, see Table 9 for result.

	Sample				
Time [min]	**1 [%]**	**2 [%]**	**3 [%]**	**4 [%]**	**5 [%]**
0	0.002	0.001	0.001	0.001	0.001
1	0.098	0.038	0.251	0.168	0.414
2	0.339	0.158	0.714	0.524	1.1

Table 9. Result from the second test, with constant volume, to determine the affects of measuring.

The third test was performed with a constant volume and flushed down to an initially value of 0.001%. In Table 10 the number in the left column indicates the time and the letter indicates the measurement.

	Sample				
Time [min]	**1 [%]**	**2 [%]**	**3 [%]**	**4 [%]**	**5 [%]**
0a	0.004	0.005	0.005	0.007	0.006
0b	0.002	0.003	0.003	0.004	0.004
0c	0.002	0.003	0.003	0.003	0.003
1a	0.007	0.008	0.01	0.011	0.01
1b	0.005	0.006	0.007	0.008	0.007
1c	0.005	0.005	0.006	0.007	0.006
2a	0.003	0.009	0.009	0.012	0.011
2b	0.003	0.007	0.007	0.009	0.008
2c	0.003	0.006	0.007	0.007	0.007

Table 10. Result from the third test to determine if a high value (20.9%) affects the next measurement value.

The fourth test was performed with a constant volume and flushed down to an initially value of 0.001%. See Table 11 for result.

	Sample				
Time [min]	***1 [%]***	***2 [%]***	***3 [%]***	***4 [%]***	***5 [%]***
0	0.001	0.001	0.001	0.001	0.001
1	0.001	0.001	0.002	0.001	0.001
2	0.001	0.001	0.002	0.002	0.001
3	0.001	0.001	0.002	0.002	0.001

Table 11. Result from when the check valves had been changed to bended pipes.

The fifth test was performed in a similar manner as the fourth but with the bended pipes exchanged to straight pipes. The result can be seen in Table 12.

	Sample			
Time [min]	***1 [%]***	***2 [%]***	***3 [%]***	***4 [%]***
0	0	0	0	0
1	0	0	0	0
2	0	0	0	0
3	0	0	0	0

Table 12. Result from when the bended pipes had been exchanged to straight pipes.

A sixth test was performed with check-valves, constant volume and with a newly calibrated Dansensor. The result can be seen in Table 13.

	Sample				
Time [min]	***1 [%]***	***2 [%]***	***3 [%]***	***4 [%]***	***5 [%]***
0	0.001	0.001	0.001	0.001	0.001
1	0.001	0.001	0.002	0.001	0.001
2	0.001	0.001	0.002	0.002	0.001
3	0.001	0.001	0.002	0.002	0.001

Table 13. Result from a last test with constant volume and straight pipes changed to check valves with the newly calibrated Dansensor.

5.1.4 Result of test; Smallest detectable volume

A first pre-test was performed to find a suitable waiting time for the test. The result from the test can be seen in Table 14.

	Sample			
Time [s]	***1 [ppm]***	***2 [ppm]***	***3 [ppm]***	***4 [ppm]***
30	1410	2180		
60	1540	1300	1480	1250
90	1870	1630	1770	
120	1770	1690	1660	1580

Table 14. Result of the pre-test to determine a suitable waiting time between injecting air and performing a measurement.

The conclusion of the test was that two minutes is an appropriate waiting time. The test to find the smallest detectable volume was performed in the manner described under heading 4.1.5.5. The result can be seen in Figure 22.

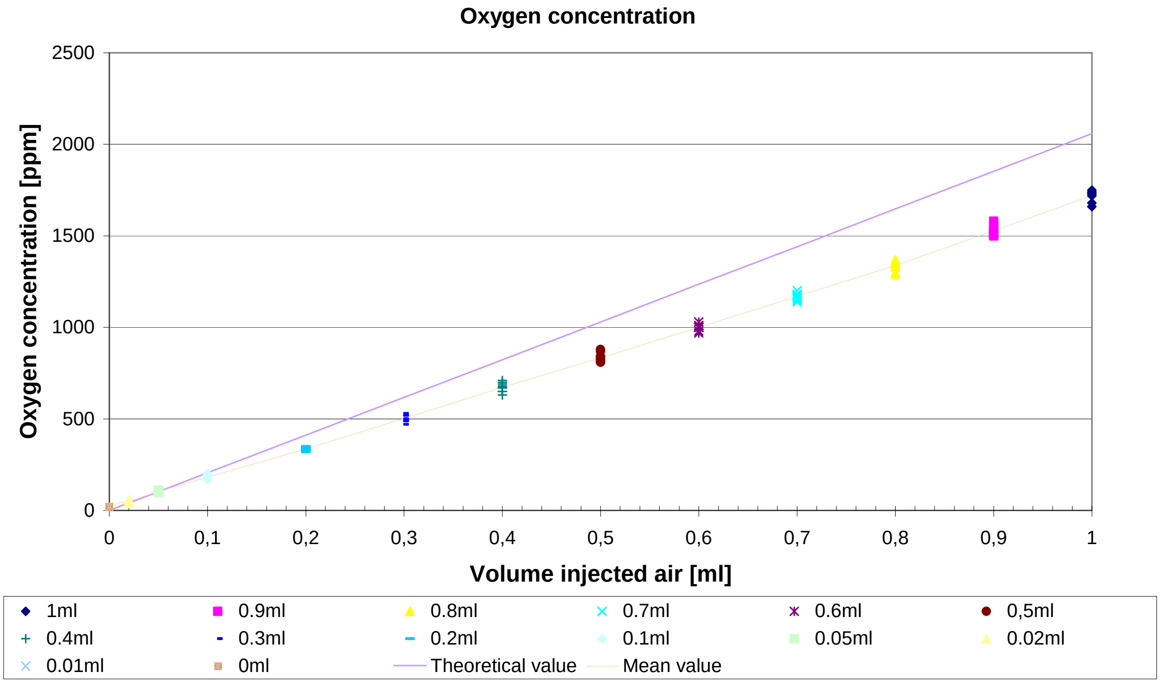


Figure 21 shows the result from the test to find the smallest detectable volume. Waiting time used was two minutes. See Appendix 3 and Appendix 4 for larger graph and measurement values

Smallest volume that was detectable with this equipment and this setup was 0.01ml of injected air in a 101.5ml volume. This value was used to estimate the time it can leak before the equipment can detect the leakage. The graphs below show the result from the calculations with different pressures and leak-sizes.

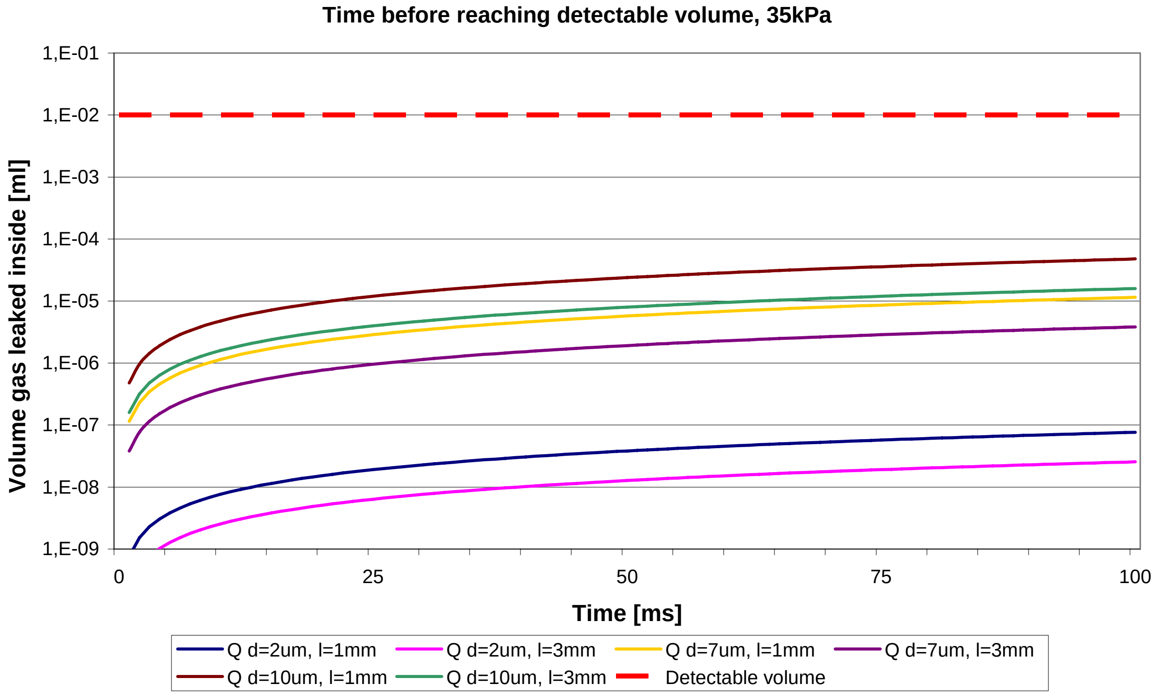


Figure 22 shows the volume gas that leaks inside during100ms with a specific volume flow and a pressure difference of 35kPa. Notice the use of logarithmic scale.

Figure 23 shows that it was clear that the volume flow in a temporary leak with these hole-sizes does not add up to the critical volume within the time margin of a temporary leak. It could be interesting to see what leak size is needed with the time-limit and detectable volume given.

This method can be implemented with tailor made sensors for oxygen or other gases that have an accuracy and detection level far better than the one used. To see if other sensors are more likely to solve the problem they are included in the following calculations. The purpose of these calculations is to answer the question "If the duration time of a temporary leak and the detection limit of the sensor are known, what leak-size can be detected?"

Given data:

Leakage time, t	4 ms
Leak length, l	1 & 3 mm
Detection level, Dl	1, 5, 10 ppb & 10 ppm
Pressure difference, ΔP	5 & 35 kPa
Dynamic viscosity at 20°C, μ	18 μPa*s
Gas concentration, C	20%
Test volume, V	100ml

A first step is to calculate what volume of the measurable gas that needs to leak inside in order to detect it. Poiseuilles equation for laminar flow through pipes and the relation between volume flow and volume divided by time are then used to find an equation for the leak-radius:

$$V_{\det ectable} = \frac{V * Dl}{C}$$

$$Q = \frac{\pi r^4}{8\mu l}\Delta P = \frac{V_{\det ectable}}{t} \Rightarrow$$

$$r = \sqrt[4]{\frac{8 * V_{\det ectable} * l * \mu}{t * \Delta P * \pi}}$$

Where r is the leak radius (m). The result of the calculations can be seen in Table 15.

Sensor accuracy	Detectable volume	Length of leak	Pressure differential	Leak radius	Leak diameter
DI	Vdetection [m3]	l [m]	∆P [Pa]	r [m]	d [µm]
1 ppb	*5.0E-13*	*0.001*	*5000*	*5.8E-06*	**11.6**
1 ppb	*5.0E-13*	*0.001*	*35000*	*3.6E-06*	**7.2**
1 ppb	*5.0E-13*	*0.003*	*5000*	*7.7E-06*	**15.3**
1 ppb	*5.0E-13*	*0.003*	*35000*	*4.7E-06*	**9.4**
5 ppb	2.5E-12	0.001	5000	8.7E-06	**17.4**
5 ppb	2.5E-12	0.001	35000	5.4E-06	**10.7**
5 ppb	2.5E-12	0.003	5000	1.2E-05	**22.9**
5 ppb	2.5E-12	0.003	35000	7.0E-06	**14.1**
10 ppb	*5.0E-12*	*0.001*	*5000*	*1.0E-05*	**20.7**
10 ppb	*5.0E-12*	*0.001*	*35000*	*6.4E-06*	**12.7**
10 ppb	*5.0E-12*	*0.003*	*5000*	*1.4E-05*	**27.2**
10 ppb	*5.0E-12*	*0.003*	*35000*	*8.4E-06*	**16.7**
10 ppm	5.0E-09	0.001	5000	5.8E-05	**116.4**
10 ppm	5.0E-09	0.001	35000	3.6E-05	**71.5**
10 ppm	5.0E-09	0.003	5000	7.7E-05	**153.1**
10 ppm	5.0E-09	0.003	35000	4.7E-05	**94.2**

Table 15. Result from calculations of detectable leak-sizes with different configurations of pressure, leak length and detection level of sensor.

5.2 Result, test to investigate influence by diffusion

5.2.1 Result from initial test to fill and seal packages

The result from the first initial test to fill and seal packages with the sealing rig can be seen below in Table 16.

Package	Time [min]	O2 [%]	
1	2	0.348	
2	3	0.208	
3	4	0.708	
4	5	0.122	
5	2.5	0.128	(*)

Table 16. Result from the first test with track B packages with different waiting times. (*) was de-aerated before it was placed in the sealing rig.

There is not a result from many packages due to a big loss of packages while trying to get the sealing process to work. To find the difference in time between emptying a package filled with water respectively without, a small test was performed. Result can be seen in Table 17.

Package	Time [min]	O2 [%]
Empty	2	0.002
Full	11	0.003
Sealed		0.42

Table 17. Result from a small test to see differences between evacuating a full respectively an empty package from oxygen. Package with water were sealed to see influence of sealing process.

5.2.2 Result from de-aerating water

The result from the first test evaluating the efficiency of different methods to de-aerate water can be seen in Table 18.

Liquid	**Temperature [°C]**	**O_2 -level [mg/L]**	**Time [min]**
Tap water	14.4	10.6	
Tap water	23.6	8.45	
Tap water	45.5	6.9	
Water bubbled with N_2	19.7	3.13	6
Water bubbled with N_2	20	0.46	~15
Water bubbled with N_2	20	0.45	~20
Water bubbled with N_2	20.2	0.23	~25
Boiled water	43.8	3.2	

Table 18. Result from the initial test when choosing method to de-aerate the water from oxygen in the packages.

The previous test resulted in that Nitrogen were used to de-aerate water. Different nozzle-types were tried out, the result can be seen in Figure 24.

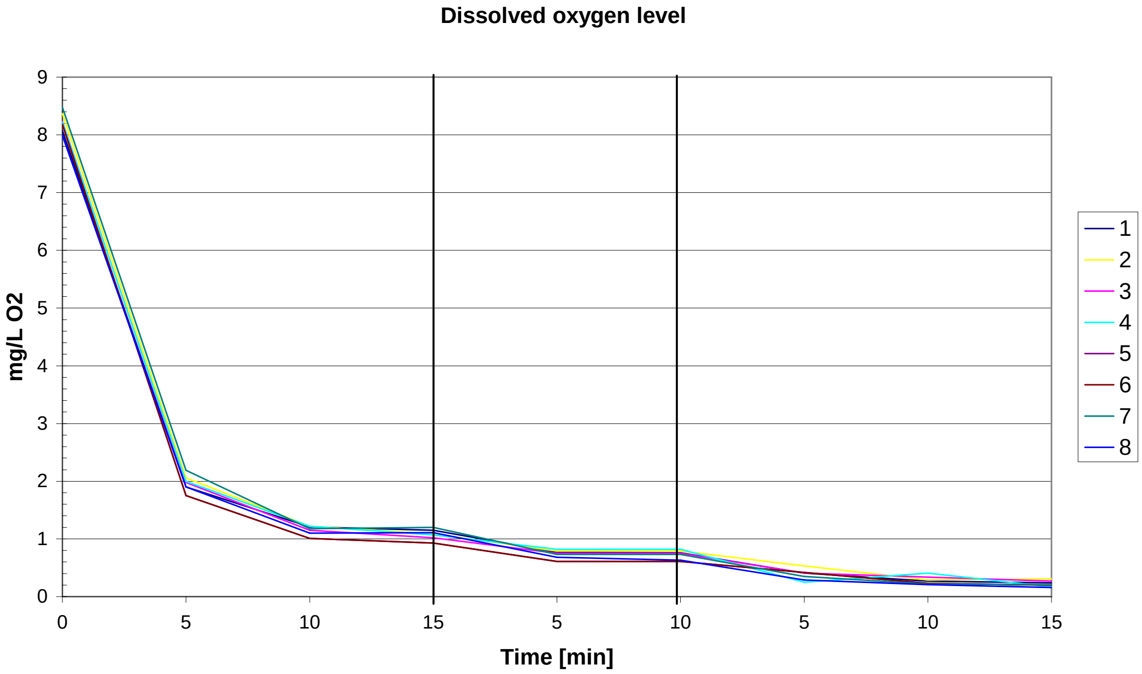


Figure 23 . The DO-level changes when using different nozzle types. The vertical lines indicate when the nozzle-design was changed.

During the same test, the temperatures for the packages were logged, in order to see if the initial temperature affects the test. Result can be seen in the table below.

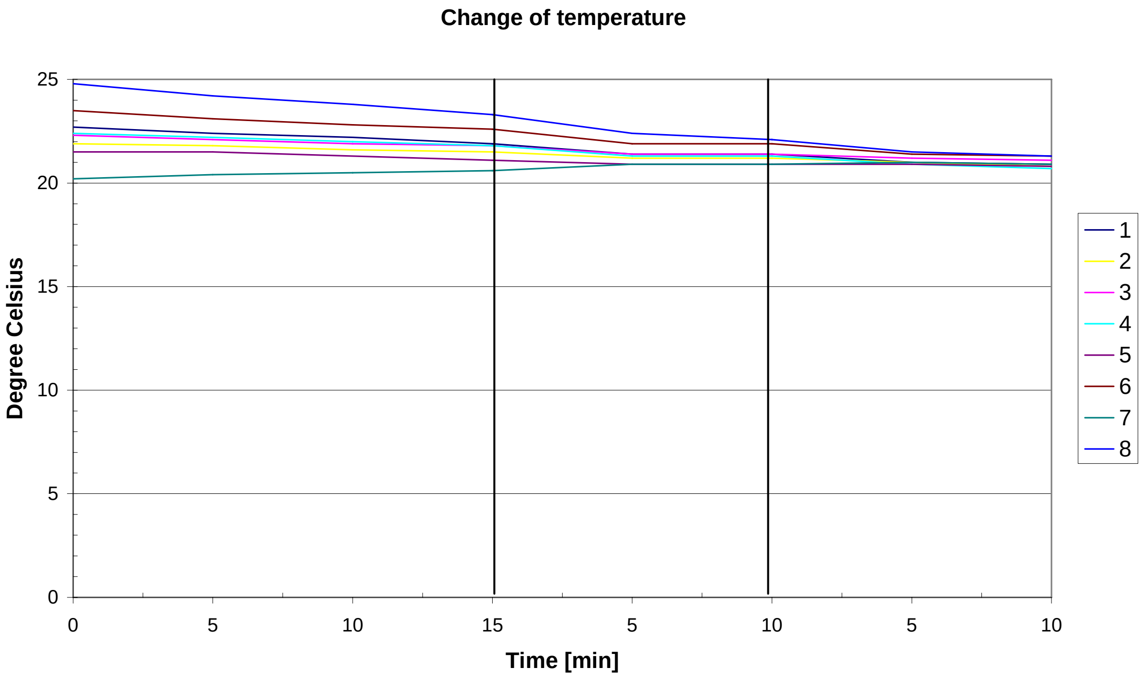


Figure 24 Temperature changes while de-aerating the water. The lines indicate when the nozzle-design was changed.

5.2.3 Result from filling and testing packages

A test to improve the filling ant sealing process was performed. Different combinations of gas flows and flushing times were tried. Result can be seen in Table 19.

Package	***Time [min]***	***O2 [%]***	***Flow [L/min]***	***Gas [on/off]***	***Side flow***
1	1.5	0.026	100	off	off
2	1	0.025	100	off	off
3	2	0.435	100	on	on
4	1	0.4	60	on	on
5	1	0.313	100	on	on
6	1	0.536	100	on	on
7	1	0.136	100	on	off

Table 19. Result from different combinations of using side flow, flow and gas on or off when pulling the nozzle tool up.

When the gas combination was evaluated, different flows and waiting times had to be tried in order to achieve a steady initial head-space environment. The result can be seen in Table 20.

Package	Time [min]	O2 [%]	Flow [L/min]	DO [mg/L]
-	1	0.11	50	0.28
-	2	0.329	10	-
-	1.5	0.097	100	0.56
-	1.5	0.25	100	-
-	1.5	0.18	100	-
-	2	0.106	30	-
13	2	0.108	30	0.6
8	2	0.11	30	0.38
52	2	0.092	30	0.6
17	2	0.108	30	0.6
19	2	0.088	30	0.58

Table 20. Result of test when flows and waiting times were varied in order to find a good steady initial value. Real test starts when package get numbered.

After finding a sealing process that was stable enough, the test-packages were sealed and stored for various times. Before they were opened the headspace concentration was measured. Result can be seen below.

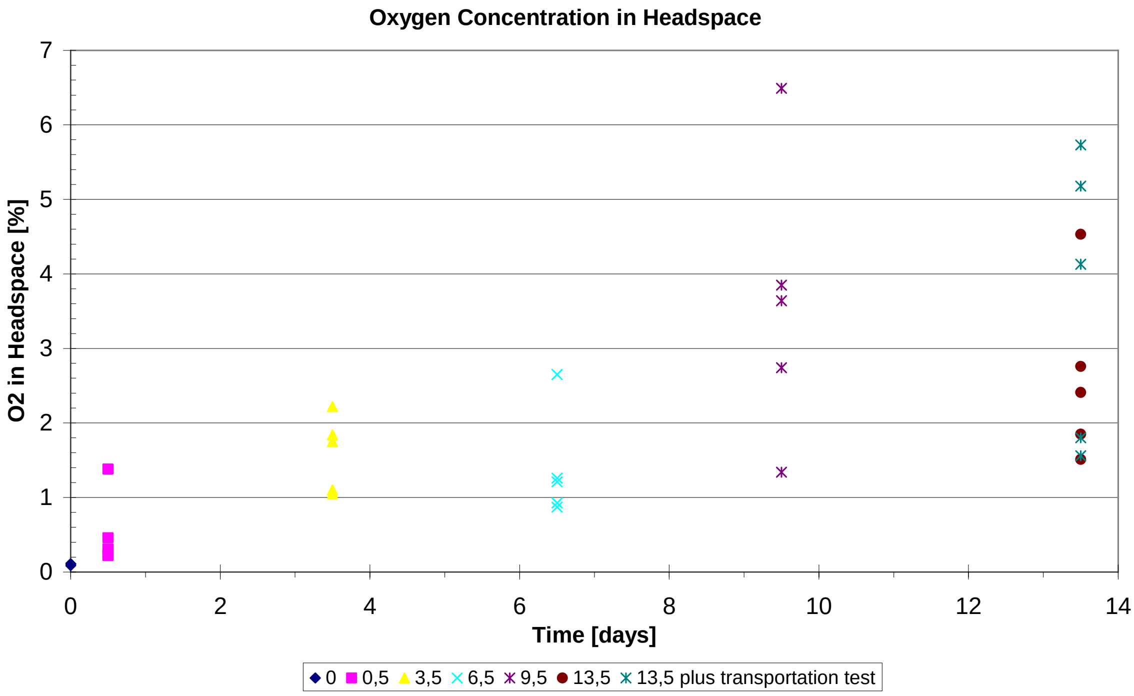


Figure 25. Measured values of the oxygen concentration in the headspace over time.

When the oxygen concentration in the headspace was measured, the top of the package was cut of and the DO-level measured. Result can be seen in Figure 27.

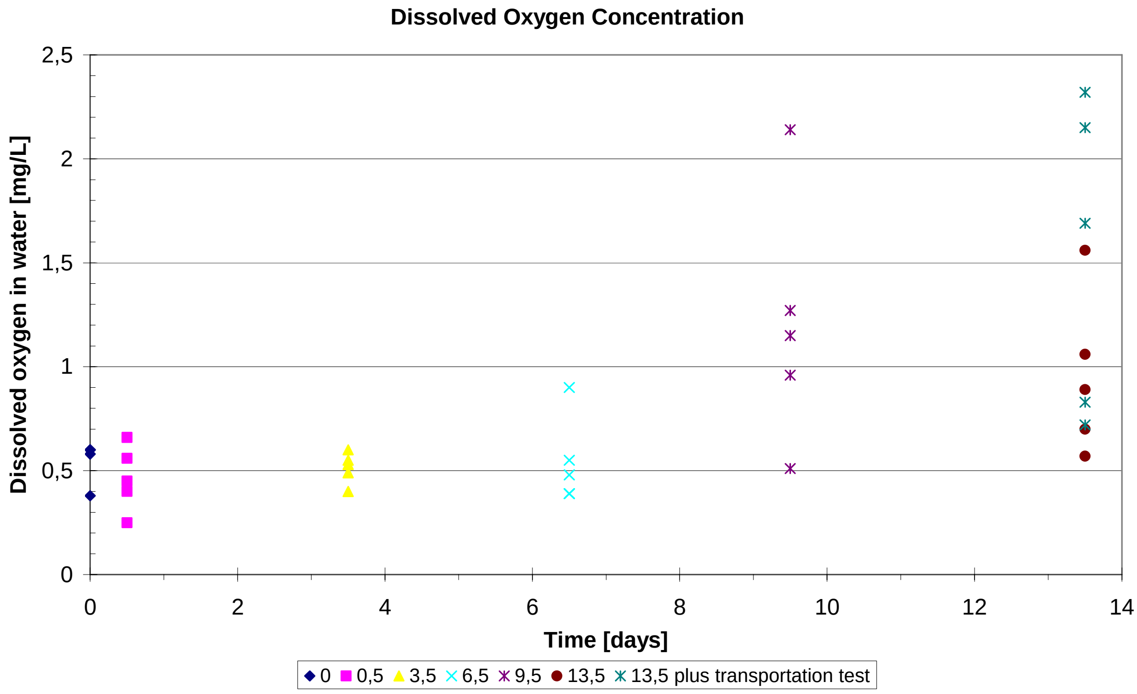


Figure 26. Measured DO concentration in the water over time.

How the DO-level changes is more interesting than the actual level after a certain time. Therefore the difference is shown in Figure 28.

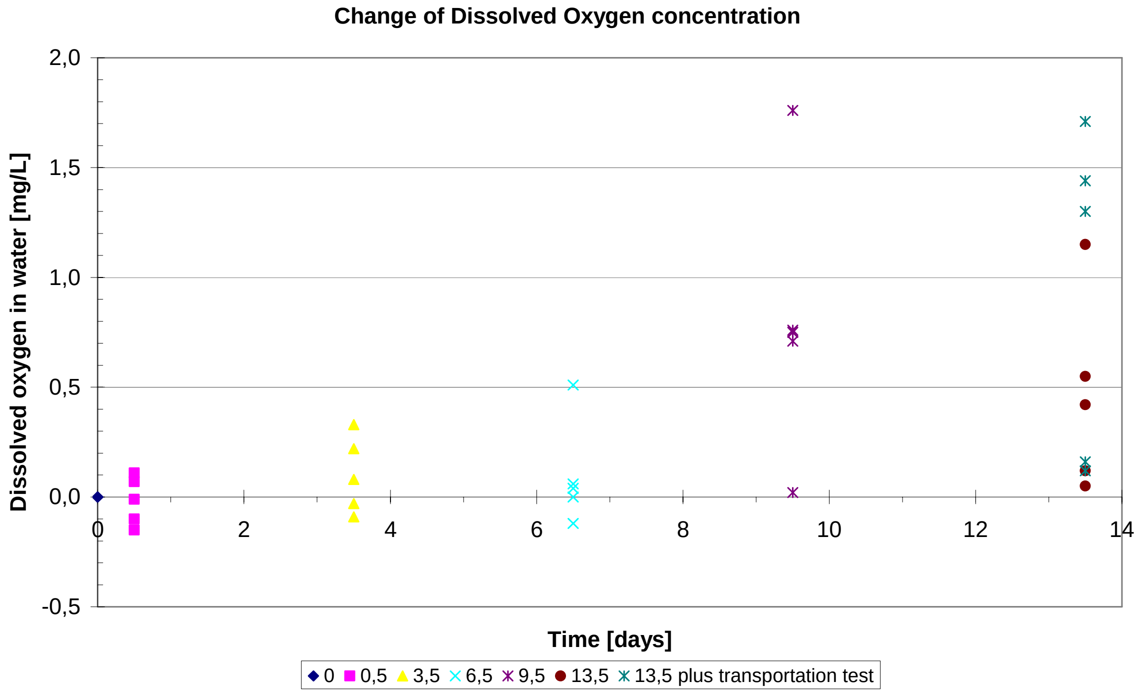


Figure 27. Change of DO concentration in packages after a certain time.

The goal of the test was to establish how much the oxygen concentration has increased over time. The total amount of oxygen that has been getting in to the package can be calculated by first calculating the mass oxygen, m_{O2} (g), inside the package before and after. This is recalculated to a volume V (mL) by the following equations;

$$m_{O_2} = \frac{C_{o_2liq} * V_{liq}}{1000} + \frac{C_{O_2HS} * V_{HS} * \rho_{O_2}}{100}$$

$$\Delta V_{O_2} = \frac{m_{O_2} - m_{O_2Initial}}{\rho_{O_2}} * 1000$$

Where C_{O2liq} is the concentration oxygen in water (mg/L), CO_{2HS} is the concentration oxygen in the headspace (%), Vliq and VHS is the volume liquid respectively headspace (L) and ϱ is the density of oxygen (g/L). The result of the calculations can be seen below.

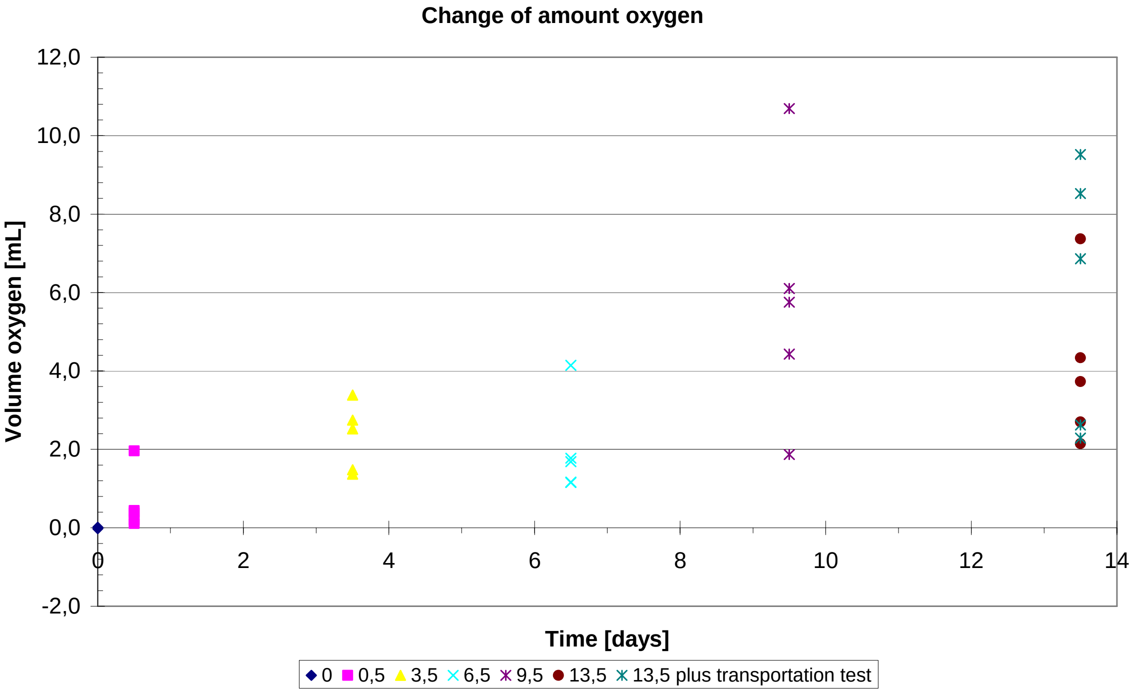


Figure 28. Total amount of oxygen that has been getting in to the packages calculated from measurement values.

5.2.4 Calculations

The calculations to investigate whether the oxygen diffuse from the water to the headspace or vice versa could be made when the measurement values are received.

Data;

$P_{air} = 1.013bar$

$T = 296K$

$\rho_{H_2O,T} = 999kg/m^3$

$\rho_{O_2,T} = 1.184kg/m^3$

$M_{O_2} = 31.999 * 10^{-3} kg/mol$

$M_{H_2O} = 18.016 * 10^{-3} kg/mol$

$C_{O_2,HS} = 0.1\%$

$C_{O_2,liq} = 0.2mg/L$

The above measured values of oxygen concentration in liquid respectively headspace were retrieved during tests when emptying packages of oxygen. The concentration was measured before any impact of diffusion. The purpose of the calculations is to compare, for a given oxygen concentration in air, the calculated saturated dissolved oxygen concentration in the liquid with a measured value. Calculation based on oxygen concentration from headspace, see "4.2.3 Calculations" for explanation of calculations.

$$P_{i,gas} = C_{O_2,HS} * P_{air} = 0.1*10^{-2} *1.013 = 1.013*10^{-3} bar$$

$$H = 38000 + \frac{45000-38000}{300-290} * (296-290) = 42200 bar$$

$$\gamma_{O_2,H_2O} = \frac{P_{i,gas}}{H} = \frac{1.013*10^{-3}}{42200} = 2.401*10^{-8}$$

$$N_{H_2O} = \frac{\rho_{H_2O,T}}{10^3 * M_{H_2O}} = \frac{999}{10^3 *18.016*10^{-3}} = 55.451 mol/L$$

$$N_{O_2} = \gamma_{O_2,H_2O} * N_{H_2O} = 2.401*10^{-8} *55.451 = 1.331*10^{-6} mol/L$$

$$C_{m,O_2} = N_{O_2} * M_{O_2} *10^6 = 1.331*10^{-6} *31.999*10^{-3} *10^6 = 0.043 mg/L$$

The result shows that the calculated value is smaller than the measured value. The calculations are made based on oxygen concentration from the water to see the calculated oxygen concentration in headspace.

$$N_{O_2} = \frac{10^6 * C_{O_2,liq}}{M_{O_2}} = \frac{10^6 *0.2}{31.999*10^{-3}} = 6.250*10^{-6} mol/L$$

$$\gamma_{O_2,H_2O} = \frac{N_{O_2}}{N_{H_2O}} = \frac{6.250*10^{-6}}{55.451} = 1.127*10^{-7}$$

$$P_{O_2} = \gamma_{O_2,H_2O} * H = 1.127*10^{-7} *42200 = 4.757*10^{-3} bar$$

$$C_{O_2,HS} = \frac{P_{O_2}}{P_{air}} = \frac{4.757*10^{-3}}{1.013} = 4.696*10^{-3} = 0.470\%$$

The calculations show that the water contain a higher concentration of oxygen, and therefore oxygen will diffuse from the water to the headspace.

6 DISCUSSION/CONCLUSIONS

6.1 Evaluation test of oxygen sensing equipment

6.1.1 Calculations

Some assumptions were made to simplify the calculations. The flow through the leakage was assumed to be viscous and laminar. This was not a correct assumption for leaks with a diameter smaller than 7μm, but it should be considered that the critical leak size is approximately 7μm and that the flow was close to viscous even for smaller leak sizes. Only calculations considering the flow are directly affected. Another assumption made for the calculations was the ideal gas properties of air, which is correct when the gas is under normal conditions and not close to liquefaction. The geometry of the leak was assumed to be circular. Calculations were then made for different diameters and lengths. With the aid of FEM analyzes it might be possible to predict the geometry more precisely in the future to get more accurate analyze. The calculations in this report does not concern any start up time for the flows, the flows were assumed to be steady instantaneously.

6.1.2 Tests

6.1.2.1 Flushing time test

The flushing time test showed that it was not convenient to find a specific waiting time because of variations in the oxygen level. Instead a level of 0.001% was found to be a good initial value for the tests and the container was flushed, between every measure, until the level was reached. A problem that occurs when using a specific value as initial value is that it is hard to distinguish between 0 and 0.0014%. This affects the tests to a large extent when measuring at low concentrations.

6.1.2.2 Affect from sample

A problem that permeated the whole test was that it was very hard to keep the container tight. Found problem areas;

- If the flow was too high when flushing the container, the created over-pressure will cause the septum to leak. This was solved by cleaning the surface with spirituous and even out unevenness with sandpaper. Silicone grease was used to help tighten around the septum.
- The tightening between check valve and container. Silicone grease used to tight.
- The tightening between hose and check valve. Silicone grease used to tight.
- The regulator on the nitrogen gas-cylinder was malfunctioning which resulted in a small flow even when the regulator was closed. Change of regulator and adding check valve solved the problem.
- The attachment between the filter and the measuring-needle was leaking. This was solved by changing the needle.

Leaks were detected both by vision and by using hydrogen as a tracer gas and searching for leaks with a hydrogen sniffer. The Problem with the regulator was detected by connecting a hose that was held under water while the regulator was closed. Bubbles appeared which indicated a leakage of the regulator.

From the first test it was observed that the oxygen level stayed quite steady while the pressure-differential was zero, but the second test pointed out the sensitivity of an under-pressure inside the container. The under-pressure, created by the sample extracted for the measurement, resulted in big leakages that were not detected before.

When the Dansensor measured in a high oxygen concentration environment, the next measurement was affected. This was showed by the third test. When measuring three times in a row, the first measurement was higher than the two following. This indicated that there were still traces of oxygen in the hose of the measuring equipment that was not completely removed. The oxygen level inside the container increased after every insertion of the measuring needle. This indicated either a leak or that oxygen was brought into the container by the needle.

The fourth test indicated that bended pipes would be better than check valves. They were not used later though because silicone grease was used to tight the check valves. The fifth test was aborted due to values lower than the Dansensors detection limit. The used Dansensor was exchanged to a newly calibrated Dansensor that was used for all further tests.

6.1.2.3 Smallest detectable volume

The first part of this test was to find a suitable waiting time. The test showed that after a waiting-time of 30 seconds, the values varied a lot and the result changed a lot on the display of the Dansensor before a result was shown. It was first after two minutes waiting-time a steady result was achieved.

In the real test it was found that the smallest detectable volume air in a container of 101.5ml was 0.01ml. The result does not fully match the theoretically calculated value. Reasons for this could be many. Maybe the injected air volume was not exact or the calculated container volume was incorrect. It might also be changes in pressure that causes the sensor to deliver a wrong measurement.

The time it takes different leakages to be detectable can be seen in Figure 23 for 35 kPa pressure-difference. It can be read from the graph that none of the presumed leak could be detected within 100ms independent of the leak length. With this equipment the detection time was far larger than for a short temporary leak. The calculation of needed leak size for various sensors and pressures gives an interesting result. With present sensor, the leaks have to be in Ø100µm area, but with a good sensor with ppb resolution the leak can be between Ø7-15µm. Because a load case will probably load the tightening enough to open it more than 7µm or not open it at all, it seems likely that a sensor with this accuracy is enough to detect temporary leakages presumed that the package is completely evacuated of the tracer gas.

6.2 Test, diffusion;

6.2.1 Calculations

To use Henry's law when calculating, Henry's constant must be estimated, which here was done by linear interpolation. This is not the most precise method and it can be seen from Table 4 that Henry's constant is not a linear function over temperature. The error that occurs can however be neglected due to that the error is smaller than a small change of temperature.

When measured values were obtained the calculations clearly shows that the oxygen diffuse from the water to the headspace. This point out the importance of evacuating the oxygen from the water.

6.2.2 Initial test

Because the sealing equipment was not designed for this test purpose, the available space for the de-aerating equipment was very limited. This resulted in problems hoisting the package in position in the rig without ruin the bottom edges, and thereby prevent a good sealing. A noticed problem issue was that the bottom edges could get uneven, resulting in a bad sealing. Many packages were broken in the method development process which was the reason for the lack of data. The packages used for this test were different those used for the "real" test.

The values received from this test had large variations and no correlation was found between flushing time and oxygen concentration. From later tests it was found that the reason for this was that the gas flow was kept on while pulling up the nozzle-tool. This can also be seen on the test were the oxygen concentration was measured seconds before the sealing process, but the concentration increased from 0.003% to 0.42%.

6.2.3 Evacuating oxygen from water

The result from the initial test, Table 17, clearly shows that temperature affects the concentration of dissolved oxygen. Boiling water almost decrease the DO-level to a third of the initial value of room temperate water. Even though boiling the water helps a lot to lower the DO-level it was not as effective as blowing the water with nitrogen. It is also practically difficult to boil and cool down 50-60 litres of water for the test. With this in concern the work continued with developing an efficient way to de-aerate the water with nitrogen. Nitrogen also has the ability to get the concentration level down more than boiling water.

The test started with open pipes as nozzles. After fifteen minutes use of the pipes the concentration had stagnated and the design was changed to a meshed net outside the pipe exhaust. The meshed net aimed to decrease the bubble size and thereby increase the nitrogen surface towards the water. This design lowers the DO-level somewhat. The design was changed to a hose with small holes, see Figure 19. This design decreases the DO-level more efficient and the design was used for the future test.

Because the test to evacuate DO from water showed that temperature affect the DO-concentration noticeable, the temperature was logged during this test. Figure 25 shows that the temperature difference for the eight packages decrease after evacuating the dissolved oxygen from the water, which also decrease the influence of temperature.

6.2.4 Filling and testing packages

From Table 18 the result from combinations of waiting times, flows, gas on or off when pulling up the nozzle-tool and side flow on or off is presented. The result showed that there should not be any flow on while pulling the nozzle tool up. This was the main factor of variations of the result. Time and flow were varied in order to get a steady initial value and to not run out of gas. The gas flow and time could have been higher and longer in order to achieve a lower steady level.

The result from the test shows large variations and a big increase of the oxygen concentrations. It can be seen that while the oxygen concentration in the headspace increase, the DO-level in some packages decrease, which support the calculations of the direction of diffusion. The total amount of oxygen increases a lot and the spread was large. Of the packages that were tested with a transport test, three of them had high values. Due to the spread it could not be determined whether they had leaked due to the test or if they had a high diffusion rate.

6.3 Conclusions from tests

The tests aimed to evaluate whether temporary leaks can be found by evacuating oxygen from a package and measure the concentration after a test, to see if the concentration has risen. The first test was evaluating the test equipment and it was found that it has a detection limit of 0.01ml injected air in a container of approximately 100ml. The second test was performed to see how diffusion could inflict this method. The result showed that large volumes of oxygen got inside the package after a few days. The second test was far from perfect and there were many issues that could be improved. The two tests were together setting the limits for the method. The Dansensor used for the test has an accuracy of 1% of the measured value, and the first test showed that a volume of 0.01ml, equal to a 30ppm raise, could be distinguished from no injected air. This can be considered as the lower detection limit for this equipment.

A first step to improve the method is to improve the conditions for the packages. Both water and headspace must have lower initial values. The water can be better evacuated by improving the nozzle and blow nitrogen through the water for a longer time. The concentration of oxygen in the headspace can be lowered by have a higher flow for a longer time. A completely new way of evacuating the oxygen might be needed to improve the result, like a long time evacuation of oxygen so that oxygen kept in the fibres is also evacuated. The method will then become more complicated and not as easy to use. A problem arising with lower values is that the concentration gradient increases, which result in a higher diffusion-rate. This must be considered when deciding a new time-limit between filling and testing packages. A more accurate oxygen sensor is also needed in order to be able to find any temporary leaks with 7 µm diameter.

The sealing process for the bottoms was practically problematic and there were many sources for faults which should be eliminated. Hoisting the package with the nozzle tool was the most critical stage of the sealing process.

6.4 Discussion and conclusions of report

6.4.1 General

In permanent leak-detection applications, it is possible that the sensitivity of physical measurements exceeds microbial challenges, but this is not the case when the leak is temporary. As mentioned before there are no sensors or other equipment, based on physical measurements, capable of practically detect a leakage with extend comparable to a single bacterium, but this will not necessary constitute a problem.

When a mechanical tightening is used on a package made out of a flexible material, it is never possible to exclude the risk of a temporary leak. Whether the leak will lead to contamination is uncertain though. When a permanent leak is present, the bacteria will have the time to grow through a liquid filled leak, while a temporary leak closes again, leaving the bacteria without this option. There is a huge difference in the conditions. Presume the size of the leak big enough to allow microbial penetration. In the case of a permanent leak, the risk of contamination remains as long as the leak is present, which might be up to a year. A temporary leak on the other hand, is only submitted for this risk during very short time intervals, during which the circumstances must be favourable for contamination.

The best possible way to approach the problem is probably to estimating the risk of a possible microbial ingression. This can be done by examining a large number of packages in the distribution chain to estimate the risk of bacteria being present around the tightening.

A test result must always be correlated to natural conditions. What good is a test if the outcome does not resemble the reality? Before making any decisions about the approach to find a feasible method for temporary leak detection this issue must be thoroughly thought through. If physical measuring methods are used, there will be a lower limit for what is possible to detect. The risk of contamination from leakages below this limit can only be estimated. Statistics or extrapolating curves from test above the limit are possible ways. What can be accepted as a lower level for the detection limit has to be evaluated. Bacterial methods are on the other hand over-sensitive because every leak big enough to allow bacterial ingression will show a positive indication, but this can be dealt with later as the main purpose here is to indicate a leak.

6.4.2 Suggested methods

The methods are presented in descending order with respect to what is considered to be the best ideas. Among methods based on physical measurements, gas sensing is the most promising concept. In the following text a sensor mounted inside a package is referred to as a SIP and equipment extracting a gas sample for analyze is referred to as an EGS. A SIP allows the gas concentration to be more or less continuously measured. A drawback with this method is that the sensitivity and accuracy probably will suffer from disturbances as the sensor is present while the package is tested. This is not the case when an EGS is used, where the analysis takes place inside the equipment under controlled forms.

Usually the accuracy is expressed as a percentage of the measured value. This means that the accuracy is superior at low gas concentrations. This favours gases not constituent in air or one of the low concentration constituents. To come around the problem of not knowing the initial conditions in the package a tracer gas not constituent in air is the best choice. The only problem is that the test has to be performed in a controlled environment (a chamber). In this environment a tracer-gas is present in a previously decided concentration. The packages can be prepared outside the chamber and the brought in for the test. The EGS still has the big disadvantage of only being able to do a single measurement. This makes the problem of distinguishing temporary leaks from possible permanent leaks or diffusion hard to solve. If a SIP is used the package can be quarantined for a while to exclude the risk of a permanent leak disturbing the measurement. Normally the diffusion-rate is low enough not to disturb the test. If all the prospects and consequences are summed up the SIP is the best choice.

The choice of tracer gas is depending on factors like safety, health aspects, equipment and the required concentration-level. The best choice from a safety and health point of view would be to use a non-toxic gas but there is a possibility that a low concentration of a toxic gas is within the health-limits, otherwise adequate measures for protection have to be made.

Calculations show, if a gas-sensor with very high sensitivity is used (one ppb) other conditions must be fulfilled if a temporary leak is to be detected. The time-lapse of the leaks existence must be at least 5ms, the pressure-differential 35kPa, the tracer-gas concentration must be 20% and the leak-diameter at least 7μm. Further on the gas must be able to traverse the length of the leak during the time it is open. This shows approximately the detection-limit for these types of measurements.

Biological methods can be used as a complement to a physical measurement. There are two possible approaches, bacteria specific placement or bioaerosols. If it is possible to fill the space between the neck and the cap with a bacteria-solution and make the solution stay in contact with the sealing while performing load-test on the package, the specific placement method is preferable due to better flexibility. The bioaerosol method requires the test to be performed in a sealed chamber.

Electric measurement with conductive medium might be possible to use. The method requires the possibility to keep conductive liquid sealed between the cap and the top. The sensitivity of this method is limited by the fact that a liquid must penetrate the tightening. There is also an uncertainty about if it is the liquid on the outside or the inside of the package that penetrates the leak, but it seems like a rather easy method to test which makes it worth trying out, at least as a preliminary method to get some quick results. If the method works further development can be performed to achieve more flexibility of the method.

Colour indicators indicating a gas not constituent in ambient air might be possible path to follow. The problem is to find chemicals or bio-material sensitive enough to create a visual difference of the pad. It is possible that a technique similar to the one used by Oxysense [44] can be used in this application to, with the difference of not using oxygen as a tracer-gas.

If a chemical is found that is able to leave visible colour-mark on the plastic material without affecting the properties, the method called scalping could be an alternative. The tightening-surface needs to be examined through a microscope because the traces would be too small to detect with the eye.

Measuring with radiation is an appealing method. The Oxysense equipment offers today a ready to use solution. The big advantage with this equipment is the possibility to make several measurements. Unfortunately the resolution is to poor for detecting small leakages, but it is definitely worth keeping an eye on the development of this method.

6.4.3 Final remarks

A possible way to deal with the problem of temporary leak-testing on mechanical sealed packages might be to use bacterial methods in the initial phase, while trying out different designs, in order to find permanent leaks and temporary leaks caused by very small loads. When the design is rigid enough to pass these first tests, a gas-based method can be used to test heavier loads. It seems more likely that the heavier test cases will cause leakages big enough allow measurements by physical methods. Generally it seems like the use of oxygen as a tracer-gas has to stand back in favour of gases not constituents of air. That is if there is no possibility calibrating the oxygen-sensors to an accuracy or resolution in higher concentration comparable to those at low concentrations. This means that the measurement must take place in a controlled environment. The fact that the leakages have such small extent makes it unlikely to believe that tests can take place outside a laboratory, unless the previously mentioned ketchup effect shows out to be accurate.

7 APPENDIX

Appendix 1. Comments about selection process

Bacteria immersion

Properties of test method:
This method is sensitive enough to detect a temporary leak.

Implementation:
Both from a working environmental point of view and practically, it is hard to apply loads to the package when it is immersed in bacteria.

Significance of result:
The significance of the test is jeopardized when applying loads to a package immersed in liquid. There is also an uncertainty about the liquid reaching the tightening area.

General impression:
This is a well proven method used to find stationary leaks, but it is not adaptable to find temporary leaks.

Bacteria specific placement

Properties of test method:
This method is sensitive enough to detect a temporary leak.

Implementation:
This is a promising idea. A problem is to make sure the bacteria are in contact with the tightening. This can be accomplished by drilling holes in the cap or using a needle to inject the liquid to the area between the cap and the neck. The package is free to handle when applying loads.

Significance of result:
One drawback is that the package probably must be kept upside down during the test. There is also uncertainty about how the drilled holes affect the properties of the cap, but if the test is performed in a proper way there should be no problems.

General impression:
This method is promising to use in temporary leak detection and can also be used to find permanent leaks.

Bioaerosols

Properties of test method:
This method is sensitive enough to detect a temporary leak.

Implementation:
The test must be conducted in a closed volume which makes it harder to apply loads. Probably some holes must be drilled in the cap to insure that the aerosol reach the tightening

area. It must also be made sure that when applying a load, the equipment does not block the cap from being exposed to the bioaerosol spray.

Significance of result:
As long as the bacteria reach the tightening area this method could work. It has to be made sure that only the area around the cap is sprayed. Otherwise it will be hard to distinguish between temporary leaks and possible permanent leaks at other location on the package.

General impression:
This method is used for permanent leak testing and might as well be applicable for temporary leaks. There is a limitation in the possibility to apply loads due to the stationary setup. In permanent leak testing there is a possibility that this method give a better result than the immersion method, considering the capability of the aerosol to reach the tightening area.

Dormant bacteria

Properties of test method:
No data available.

Implementation:
There is a great risk that the initial conditions needed are very hard to accomplish.

Significance of result:
Besides making sure that no oxygen is present in the package at the beginning of the test also a time limit for the performance of the test exists due to diffusion. If a incubation time is needed this will increase the risk of variation between the different test objects. There is no way to distinguish between temporary leaks and permanent leaks.

General impression
This method does not have any advantages in comparison to other methods.

Colour indicator

Properties of test method:
It is not established whether the required sensitivity can be obtained. There are many different substances possible to use.

Implementation:
It depends on the properties of chemicals used. One problem is though to distinguish between temporary and permanent leaks, but this problem can be dealt with by wait a short time to see if there is any influence from any permanent leaks. Generally there should be no big problems to realize this idea.
Significance of result:
If a gas, not constituent in ambient air is used, this method could work. The significance depends on the properties of the chemicals used. A demand is that the colour change is distinct enough to be seen through the cap even for a small leakage.

General impression:
This method is very appealing. It might be an easy and cheap way to indicate a leakage compared to sensors.

Burning

Properties of test method:
If proper substances are used then the sensitivity will probably be good enough.

Implementation:
It is very difficult to have high sensitivity and in the same time control the burning. There are better ways at hand.

Significance of result:
No information is available, but if the test can be performed in controlled forms, the method has potential to work.

General impression:
If the purpose of the method was to indicate the location of the leakage, this method might have been interesting.

Colour indication with enzymes

Properties of test method:
According to Patrik Adlercreutz the sensitivity needed can be achievable.

Implementation:
A common problem arises. All methods supposed to indicate a temporary leakage, based on detection of oxygen, require an oxygen level in the initial condition controlled on ppm level. This is hard to accomplish and further more the diffusion adds disturbance as well.

Significance of result:
It is uncertain if the method is accurate enough to separate diffusion from a temporary leak and unlikely that the initial condition required can be obtained.

General impression:
This method could be worth exploring for the detection of permanent leaks.

Citrus acid / pH-reactant

Properties of test method:
There are other better methods available.

Implementation:
There are other better methods available.

Significance of result:
There are other better methods available.

General impression:
This idea comes down to the measurement of pH value with a sensor. This idea does not differ much from gas detection with sensors. The only possible benefits with the method would be if the properties of the method outshine other methods or if it were much easier to implement, which do not seem likely.

Baking powder/vinegar

Properties of test method:
There are other better methods available.

Implementation:
Problems with getting the baking powder and the sensor in place make this idea difficult to implement.

Significance of result:
There is a big risk that the preparations affect the result. Part of gas will leak out in the air before it has been detected if the volume between the neck and the cap is not gas tight.

General impression:
Not worth exploring.

Aerosol, solid/gas

Properties of test method:
Whether the sensitivity will be good enough depends on the choice of substances and detection method, which have to be examined thoroughly.

Implementation:
Problems with the aerosol settling on the walls of the package or on surface of the liquid will have to be solved.

Significance of result:
A drawback with this idea is the fact that a substance is leaking out of the package, not in. One advantage with this method is that it might be possible to indicate the location of a leak.

General impression:
This idea is interesting because the variety of substances that can be used makes it possible to take advantage of different properties. The resemblance to gas, without problems with diffusion, makes this concept appealing. It is possible to reverse the method and keep the aerosol outside the package and the sensing mechanism inside. It is probably even better fitted for detection of permanent leaks.

Ferrofluid (Magnetic fluid), solid/liquid

Properties of test method:
The properties of the substances must be of a kind that makes it possible to penetrate a small leak. This depends on the choice of substances. The information about what properties are achievable with this system will have to be explored.

Implementation:
The setup will probably have to be stationary and performed in a laboratory. The ferrofluid must be present around the tightening, but otherwise there should be no problems.

Significance of result:
Once again there is the problem of detecting a substance that is leaking out of a package and not in. Benefits are that if a leakage appears, the traces of it do not disappear and there is a possibility to enhance the effect with stronger magnets.

General impression:
Interesting concept, it is always good to have knowledge about the existence of rather odd products. They might come in useful when solving a problem, but in this application it is probably not sufficient. There is a possibility that ferrofluids can be used in permanent leak detection applications. Ferrofluids are used as flexible seals, which can be useful to know when constructing fixtures for packages in leak detection applications.

Electrical measurement with conducting medium

Properties of test method:
If the implementation work, then the sensitivity would be good enough, though depending on the quality of the electronic components.

Implementation:
The major disadvantage with this method is the same as for bacteria immersion, the package must be loaded while being surrounded by a liquid. If the second option is chosen, there is an uncertainty of keeping the liquid in place. The liquid must be in contact with the tightening. The method must be further evaluated.

Significance of result:
It depends of the possibility to implement the method.

General impression:
Seems like a possible way to go. It would not take to much effort concluding whether this is a possible path to follow.

Electrical conductivity

Properties of test method:
This type of sensor is primarily used to measure the salinity in water. How the sensor reacts to oxygen is not stated, probably due to better option available.

Implementation:
There are other better methods available.

Significance of result:
There are other better methods available.

General impression:
The only possible benefits with the method would be if the properties of the method outshine other methods or if the method were much easier to implement, which do not seem likely.

Coloured liquids

Properties of test method:
It is most likely sensitive enough. The liquid will penetrate very small leaks.

Implementation:
A problem is that the package must be kept upside down during the test but otherwise there should be no problems implementing the idea.

Significance of result:
It is probably impossible to discover a small leak without unscrewing the cap. This would smear out the dye and making it even harder to detect.

General impression:
The method is available at Tetra Pak which makes it easy to test. It will be hard to find a small leakage but might work on a leakage of greater extent. If the leakage can be observed through the cap there might be a way to utilise this method. A possibility can be to add some substance to the liquid, which makes it possible using equipment to improve the sensitivity of the method.

Scalping

Properties of test method:
No data are available.

Implementation:
The package must be kept upside down during the test. There is also a risk that the liquid affect the properties of the package material.

Significance of result:
If colouring effect is good traces of small leaks can be found with the aid of a microscope.

General impression:
This might be an alternative to normal dye. The method should be rather easy to explore if a right liquid is found. If it does not solve the problem with temporary leak it might be useful for permanent leak detection.

Liquid collector at tightness area

Properties of test method:
It is most likely sensitive enough. The liquid will penetrate very small leaks.

Implementation:
There is no way to place the collector under the cap after the package is produced. There is a possibility to integrate it with the cap before the package is assembled but it will affect the test result.

Significance of result:
If there was a possibility to implement the method it might be possible to indicate a leakage, but for this application it will not fulfil the needs.

General impression:
The idea to visualize a leakage in a capillary tube, like a blood sample, is good. The whole concept of enhancing a leakage is appealing and should be considered when evaluating any method.

Traces from medium

Properties of test method:
If the proper substances are used then probably the sensitivity will be good enough. That is, there will be a detectable reaction.

Implementation:
It will be hard to put the powder in place under the cap without affect the properties of the cap. Other methods are better.

Significance of result:
To spread the powder evenly and be sure there is powder all around the tightening area might be difficult.

General impression:
This is a similar idea to “burning”. These types of ideas are probably hard to control and repeat.

Sensor mounted inside the package

Properties of test method:
There is equipment available with higher sensitivity than needed..

Implementation:
It should not be a problem. Fixating an item inside the package will affect it in some way. Further research will answer that question. The best solution will be a wireless connection otherwise the method will have to be executed in a laboratory with a stationary setup.

Significance of result:
The sample time must be short enough to allow a distinction between a temporary leak and a stationary leak or diffusion. The sensor might be sensitive to temperature differences, pressure differences or acceleration. An evaluation in each individual case will reveal what precautions need to be taken.

General impression:
This is definitely one of the most promising ideas, especially due to the possibility of real-time measuring and wireless transfer of data.

Measure traces of gas in a flow

Properties of test method:

There is equipment available with higher sensitivity than needed.

Implementation:
The setup will have to be stationary in a laboratory.

Significance of result:
There is a limitation in the possibility to apply loads due to the stationary setup.

General impression:
With the equipment available at Tetra Pak a quick evaluation can be performed.

Extract sample for analyze

Properties of test method:
The sensitivity can be very high depending on the equipment and the gas.

Implementation:
The initial conditions must be controlled to ppm level if a constituent of ambient air is to be measured, but if another gas is used the initial condition is no problem. The problem with using another gas not constituent in air is that the surrounding environment must be controlled.

Significance of result:
If the sample is taken without any gas leaking in through the septum, there should be no problem in relaying on the result. The problem lies in difficulty to know the initial gas level. Probably the result can be statistically significant if a sufficiently large number of packages are tested. Also the problem of distinguishing between temporary and permanent leaks must be taken in to account.

General impression:
This method can be worth exploring but a sensor inside the package would provide a better result.

Measuring with radiation

Properties of test method:
These methods are used widely for oxygen measurement in transparent packages. The result is at the moment depending on the package to be transparent and further more the accuracy does not fulfil the needs yet.

Implementation:
Putting a pad inside the package would not affect the result in a great extent. There should be no problems implementing this method.

Significance of result:
The result depends on the package materials possibility to transmit light with a wavelength in the range 470nm-610nm.
General impression:
This method has a great potential to be very useful as long as the accuracy will be improved.

Heat camera

Properties of test method:
The updating frequency is to slow on the cameras found on the web but if a leakage occurs the traces from the temperature differences might be present long enough to be detected. The question of resolution is hard to estimate. It probably depends of both the temperature

differential and the size of the leakage. There is a possibility that the effect of a leakage will be enhanced which will lower the demand on the resolution.

Implementation:
Probably four cameras are needed. The test will have to be performed in a lab to reach the accuracy needed.

Significance of result:
It depends of the specifications of the camera, but at the moment there are no cameras found to fulfil the needs.

General impression:
This method is better fitted to find permanent leaks. It is probably a long-shot to believe that the effect from small temporary leaks can be observed form a heat camera.

High-speed camera

Properties of test method:
As with heat camera, the conversion of camera parameters to leak-detection is difficult. In this case the resolution and the updating frequency are essential for the result. The updating frequency fulfils the demands but not the resolution. To realize this idea the equipment would have to be a combination of a microscope and a high-speed camera.

Implementation:
The test would have to be performed in a laboratory under controlled forms. The demands and properties of the equipment will most probably make it impossible to apply loads to the package.

Significance of result:
A leak in the micrometer range will probably not be possible to detect with a high-speed camera.

General impression:
This method seems to be too complicated to implement.

High pressure

Properties of test method:
Methods to measure pressure are quite well developed and sensors have a high accuracy. What must be taken in concern is that the sensitivity of the method is highly dependent of the package volume.

Implementation:
It is not practically easy to prepare a package with a sensor, liquid and a high pressure inside and then seal it.

Significance of result:
A risk with the method is that a deformation of the package can affect the pressure and thereby the test, but with a higher pressure inside the package this is probably no problem. Other disadvantages are the risk of affecting the test by applying a high pressure inside the package and that the method only confirms a leakage out of the package, which is not the same as a microbial ingression.

General impression:
Measuring pressure is not a good method when the packages are flexible, especially when temporary leaks are supposed to be found. Permanent leak would be easier because it is possible to observe the package under a longer time-span to see the trend.

Vacuum

Properties of test method:
Similar to high-pressure method

Implementation:
Similar to high-pressure method

Significance of result:
The risk of misjudging the result as a consequence of package deformation is even greater when a under pressure is applied. A benefit is though that the leakage is directed in to the package.

General impression:
Similar to high-pressure method

Pressure sensitive film

Properties of test method:
With the present technology the sensing equipment is not accurate enough and does not measure down to zero Pascal which is needed in order for the method to work.

Implementation:
The sensor film is too big and can not be placed at the proposed location.

Significance of result:
Because of the thickness and the need of a wire connected to a transmitter the result would most probably be affected.

General impression:
The sensors are not useful for this problem, but the technology could though be useful in other applications like detecting force propagation through a package when it is exposed to different tests.

Measure of light, Photomultiplier

Properties of test method:
The sensitivity is very good.

Implementation:
The sensor requires a voltage of hundreds of volt, which restrict this method to a laboratory setup. The method requires conditions that allows light to enter the package only when a temporary leak occurs, which probably will be difficult to achieve.

Significance of result:
There is a big risk that the result will be spoiled by disturbances. There is also a problem with the cap blocking the incoming light.

General impression:
Even though the sensor is very sensitive, the method is not trustworthy. If for example a gas is used for leak testing, the gas remains in the package if a leakage has occurred, light on the other hand disappears when the leak closes. This adds an uncertainty to the method. Maybe there is a possibility to use the concept in permanent leak testing where the effects are static.

Camera-film

Properties of test method:
The sensitivity is good and is changeable.

Implementation:
The preparation of the package must be done in a dark room, as well as the developing. During the test the packages can be tested without any restrictions.

Significance of result:
There is a big risk that the result will be spoiled by disturbances. There is also a problem with the cap blocking the incoming light.

General impression:
The principle is the same as for the photomultiplier and so are the problems. If the package has a design that allows the implementation of these methods they could be worth exploring. The camera-film would be rather simple to test.

Radioactivity

Properties of test method:
Sensors for measuring radioactivity are well developed and have a good accuracy. Theoretically a small volume radioactive liquid can be detected but if it is applicable to this application has to further investigated.

Implementation:
Radioactive tracers are commonly used in medical applications and are injected in the blood of human beings. Therefore it will probably be safe to work with unless there is a limitation in the exposure time. Another problem might be that the sample is ruined if even the slightest amount of the liquid is spilt.

Significance of result:
In order to trust the result it must be evaluated whether the radiation is able to penetrate the package material. A drawback with this idea is the fact that a substance is leaking out of the package, not in.

General impression:
There is a possibility that radioactive tracers can be used in temporary leak detection application. It has been used for permanent leak detection but if it is adaptable for this application has to be further evaluated.

X-ray

Properties of test method:
According to companies working with X-ray for food-industry, the detection limit for X-ray are objects with a diameter down to 0.3mm, at the moment, which is much too large for this application.

Implementation:
The implementation depends on the equipment, which not fulfils the needs.

Significance of result:
If the properties were fulfilled the demands, the significance would have been dependent on the resolution. This idea suffers also from the fact that a substance is leaking out of the package instead of the opposite.

General impression:
The method is not interesting due to the detection level of present X-rays.

Light detection with small camera

Properties of test method:
The camera must either have a very high resolution in order to find leaks with a size of only a few microns or be very light sensitive to detect the light from the leak. Further on the camera must be of a size that fits in a package. This has not been found and is very unlikely to be found.

Implementation:
The camera must be able to observe the whole tightening in a 360 degree angle. It must sustain vibrations and heavy accelerations.

Significance of result:
If the camera is to find the light that shines through the leak, the same problems as for the photomultiplier are encountered. If it were to produce an image of the leak a combination of a microscope and a high-speed camera will have to be used and a light source is needed inside the package. Neither of the options will probably be useful.

General impression:
The method is not worth evaluating.

Ultra Sound

Properties of test method:
It is important that the measurement equipment have a resolution high enough to detect holes in the micrometer range, which not seem to be available at the moment.
Implementation:
When a package is submitted to loads it will move. It is unlikely that this measuring method would work if the package is not still.

Significance of result:
The test result would probably be shattered with noise.

General impression:
This method is not worth evaluating, at least not for temporary leaks.

Detection of specific sound

Properties of test method:
Even though microphones and signal filtering are well developed it is hard to imagine this idea would fulfil the demands. The method is aiming to find an opening with a diameter of 10μm in a material that is not homogeneous and moving, additionally there are sounds created when the load is applied that will interfere with the measurement.

Implementation:
When the package is prepared there should not be any restrictions of testing the package.

Significance of result:
It will not be possible to distinguish between different cases and knowing that a leak in fact has occurred.

General impression:
This is a method that is unlikely to work.

Detection of sound from leakage

Properties of test method:
Even though there is good equipment to detect leakages through noise, the flow rate from these leakages is most probably too low to create detectable noise.

Implementation:
The method would be difficult to implement.

Significance of result:
The result would not be trustworthy due to the low leakage rate appearing from temporary leakages.

General impression:
This method is not worth evaluating.

Strain gauge

Properties of test method:
A deformation is not equal to a leak.

Implementation:
Applying the strain gauge method practically is difficult.

Significance of result:
A deformation is not equal to a leak.

General impression:
This method is not worth evaluating.

Strings that brake at deformation

Properties of test method:
A deformation is not equal to a leak.

Implementation:
Applying strings inside the tightening practically is difficult.

Significance of result:
A deformation is not equal to a leak.

General impression:
This method is not worth evaluating.

Modified cap

Properties of test method:
This method is only an aid for other methods and has no properties itself.

Implementation:
This idea is very general and might work in some cases. Drilling a small hole to inject bacteria would probably be no problem while other ideas might ruin the cap.
Significance of result:
As long as the damage on the cap does not affect the result it would be possible.

General impression:
It is probably not easy to estimate the affect, a damage on the cap, would have on the significance.

Particle movement

Properties of test method:
A leak does not necessary cause the smoke to move.

Implementation:
It would be very hard accomplish practically.

Significance of result:
Probably the smoke would move constantly which would make it hard to distinguish a leakage.

General impression:
This method is not worth evaluating.

QCM

Properties of test method:
The sensor is not sensitive enough to detect gas, but if some other substance was to be detected it might work. Bacteria or some kind of aerosol could be used.

Implementation:
The sensor it self would not be a problem to mount.

Significance of result:
It depends on the approach of the method.

General impression:
This is an interesting method that might be useful to look in to. It demands some research though.

Biosensor

Properties of test method:
A biosensor is defined by the structure of the sensor. It has to contain a biological or biochemical reactant. Nothing can be said about the properties due to the general structure of this idea.

Implementation:
There should generally not be any bigger problems in mounting a sensor inside the package.

Significance of result:
It depends on the structure of the sensor.

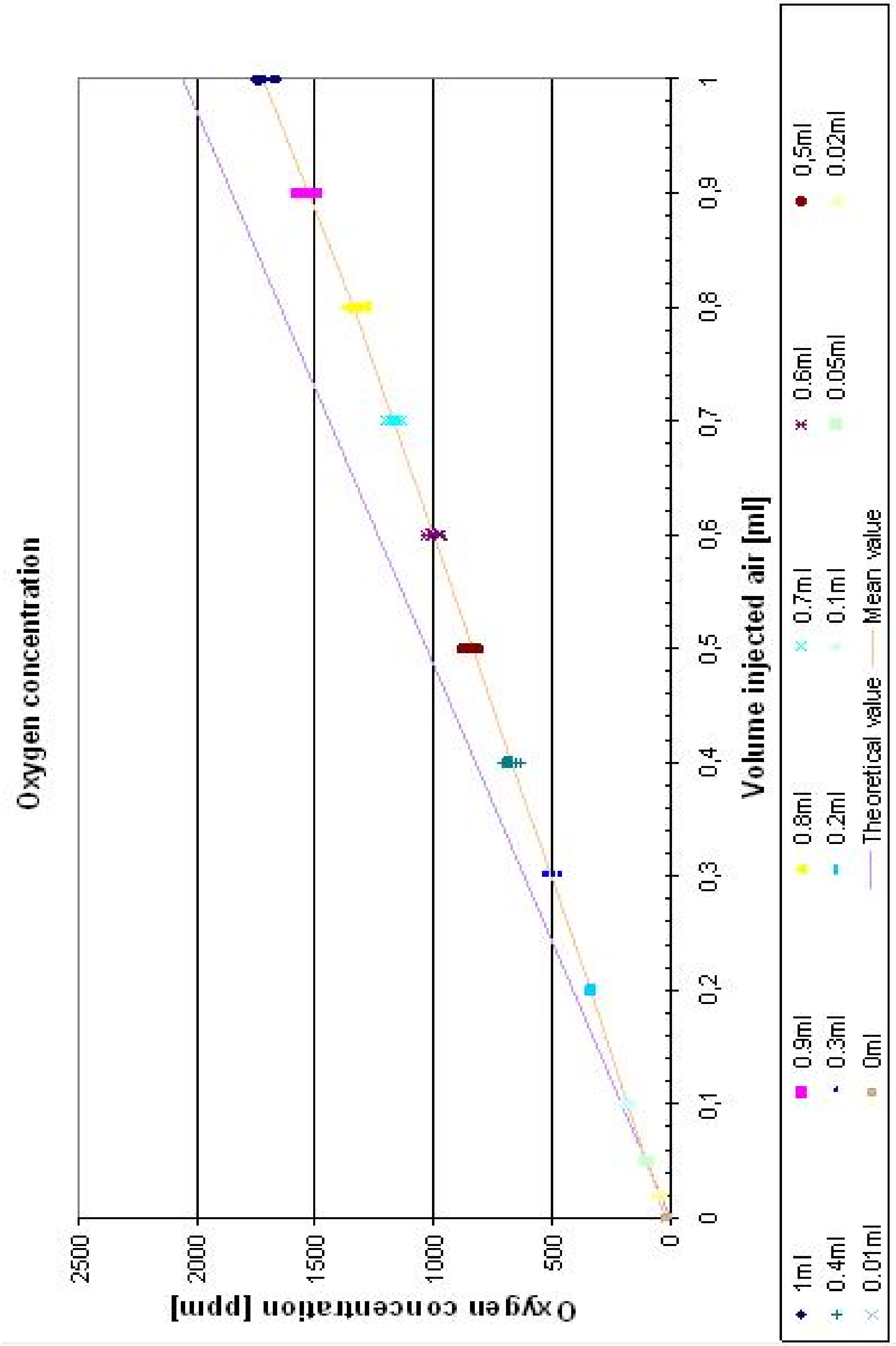
General impression:
It might be interesting to look in to this field. There is a possibility to tailor these sensors to the application, but at the moment there are better methods available.

Appendix 2. Emerging techniques

There is always an interest in finding new enhanced methods for gas detection. Ongoing research is usually of a general nature and is not necessarily aiming for gas detection but the following concepts are mentioned in this context. This section is included in order not to risk excluding any information about leak testing in future reviews of this document.

- Micro electromechanical systems
- Nanometal oxides
- Carbon nanotubes
- Quantum dots and wire
- Micro (optical) spectrometer
- Micro mass spectrometer
- Micro gas chromatography
- Widely tuneable solid-state lasers
- Differential ion mobility spectroscopy (DMS,FAIMS)
- Polarographic oxygen sensor
- Thermal conductivity
- Non dispersive infrared (NDIR)
- UV fluorescence

Appendix 3. Graph, oxygen concentration, detection level test



Appendix 4. Table, oxygen concentration, detection level test

Test	**Volume [ml]**	**Result [ppm]**	**Volume [ml]**	**Result [ppm]**	**Volume [ml]**	**Result [ppm]**	**Volume [ml]**	**Result [ppm]**
1	1	1730	0.9	1580	0.8	1340	0.7	1180
2	1	1740	0.9	1550	0.8	1350	0.7	1160
3	1	1730	0.9	1510	0.8	1290	0.7	1170
4	1	1740	0.9	1530	0.8	1300	0.7	1170
5	1	1720	0.9	1510	0.8	1360	0.7	1200
6	1	1730	0.9	1520	0.8	1330	0.7	1180
7	1	1680	0.9	1560	0.8	1350	0.7	1140
8	1	1660	0.9	1500	0.8	1370	0.7	1180
9	1	1730	0.9	1520	0.8	1350	0.7	1150
10	1	1750	0.9	1500	0.8	1340	0.7	1170
mean value	*1*	*1721*	*0.9*	*1528*	*0.8*	*1338*	*0.7*	*1170*
Theoretical value	*1*	*2059*	*0.9*	*1853*	*0.8*	*1647*	*0.7*	*1441*

Test	**Volume [ml]**	**Result [ppm]**	**Volume [ml]**	**Result [ppm]**	**Volume [ml]**	**Result [ppm]**	**Volume [ml]**	**Result [ppm]**
1	0.6	1010	0.5	820	0.4	650	0.3	490
2	0.6	1000	0.5	870	0.4	670	0.3	490
3	0.6	980	0.5	840	0.4	680	0.3	470
4	0.6	1000	0.5	830	0.4	670	0.3	500
5	0.6	1000	0.5	810	0.4	630	0.3	490
6	0.6	1000	0.5	810	0.4	650	0.3	520
7	0.6	970	0.5	820	0.4	670	0.3	520
8	0.6	1000	0.5	830	0.4	690	0.3	520
9	0.6	1030	0.5	840	0.4	710	0.3	500
10	0.6	1010	0.5	880	0.4	700	0.3	530
mean value	*0.6*	*1000*	*0.5*	*835*	*0.4*	*672*	*0.3*	*503*
Theoretical value	*0.6*	*1235*	*0.5*	*1030*	*0.4*	*824*	*0.3*	*618*

Test	**Volume [ml]**	**Result [ppm]**	**Volume [ml]**	**Result [ppm]**	**Volume [ml]**	**Result [ppm]**	**Volume [ml]**	**Result [ppm]**
1	0.2	340	0.1	200	0.05	110	0.02	50
2	0.2	340	0.1	170	0.05	100	0.02	50
3	0.2	340	0.1	180	0.05	110	0.02	60
4	0.2	340	0.1	180	0.05	110	0.02	50
5	0.2	320	0.1	170	0.05	100	0.02	50
6	0.2	330	0.1	180	0.05	110	0.02	50
7	0.2	330	0.1	180	0.05	100	0.02	50
8	0.2	340	0.1	180	0.05	100	0.02	50
9	0.2	330	0.1	180	0.05	100	0.02	40
10	0.2	350	0.1	200	0.05	100	0.02	40
mean value	*0.2*	*336*	*0.1*	*182*	*0.05*	*104*	*0.02*	*49*
Theoretical value	*0.2*	*412*	*0.1*	*206*	*0.05*	*103*	*0.02*	*41*

Test	***Volume [ml]***	***Result [ppm]***	***Volume [ml]***	***Result [ppm]***
1	0.01	40	0	20
2	0.01	40	0	20
3	0.01	40	0	20
4	0.01	50	0	20
5	0.01	40	0	20
6	0.01	40	0	20
7	0.01	40	0	20
8	0.01	40	0	20
9	0.01	40	0	20
10	0.01	40	0	20
mean value	*0.01*	*41*	*0*	*20*
Theoretical value	*0.01*	*21*	*0*	*0*

Appendix 5. Table, diffusion test result

Nbr	***O2 in H2O [mg/L] initial***	***O2 in H2O [mg/L]***	***O2 in HS [%]. initial****	***O2 in HS [%]***	***Waiting time [days]***	***delta DO***
8	0.38	0.38	0.1012	0.11	0	0.00
13	0.6	0.6	0.1012	0.108	0	0.00
17	0.6	0.6	0.1012	0.108	0	0.00
19	0.58	0.58	0.1012	0.088	0	0.00
22	0.22	0.55	0.1012	2.22	3.5	0.33
24	0.49	0.51	0.1012	1.34	9.5	0.02
31	0.5	0.4	0.1012	0.218	0.5	-0.10
32	0.49	0.55	0.1012	1.26	6.5	0.06
33	0.14	0.25	0.1012	0.31	0.5	0.11
34	0.56	0.72	0.1012	1.56	13.5	0.16
35	0.61	2.32	0.1012	5.73	13.5	1.71
36	0.39	0.9	0.1012	2.65	6.5	0.51
37	0.47	0.89	0.1012	2.41	13.5	0.42
38	0.51	1.27	0.1012	3.85	9.5	0.76
39	0.49	0.4	0.1012	1.05	3.5	-0.09
40	0.52	0.57	0.1012	1.51	13.5	0.05
41	0.59	0.66	0.1012	1.38	0.5	0.07
42	0.51	0.39	0.1012	0.928	6.5	-0.12
43	0.31	0.53	0.1012	1.84	3.5	0.22
44	0.21	0.96	0.1012	2.74	9.5	0.75
45	0.58	0.7	0.1012	1.85	13.5	0.12
47	0.46	0.45	0.1012	0.235	0.5	-0.01
48	0.39	0.39	0.1012	0.871	6.5	0.00
49	0.44	1.15	0.1012	3.64	9.5	0.71
50	0.52	0.49	0.1012	1.1	3.5	-0.03
51	0.41	1.56	0.1012	4.53	13.5	1.15
52	0.6	0.6	0.1012	0.092	0	0.00
53	0.51	1.06	0.1012	2.76	13.5	0.55
54	0.71	2.15	0.1012	5.18	13.5	1.44
55	0.71	0.56	0.1012	0.458	0.5	-0.15
56	0.44	0.48	0.1012	1.21	6.5	0.04
57	0.71	0.83	0.1012	1.8	13.5	0.12
58	0.38	2.14	0.1012	6.49	9.5	1.76
59	0.39	1.69	0.1012	4.13	13.5	1.30
60	0.52	0.6	0.1012	1.75	3.5	0.08

** Initial value in Headspace is calculated as mean value of the first five measurements made directly after sealing the package.*

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