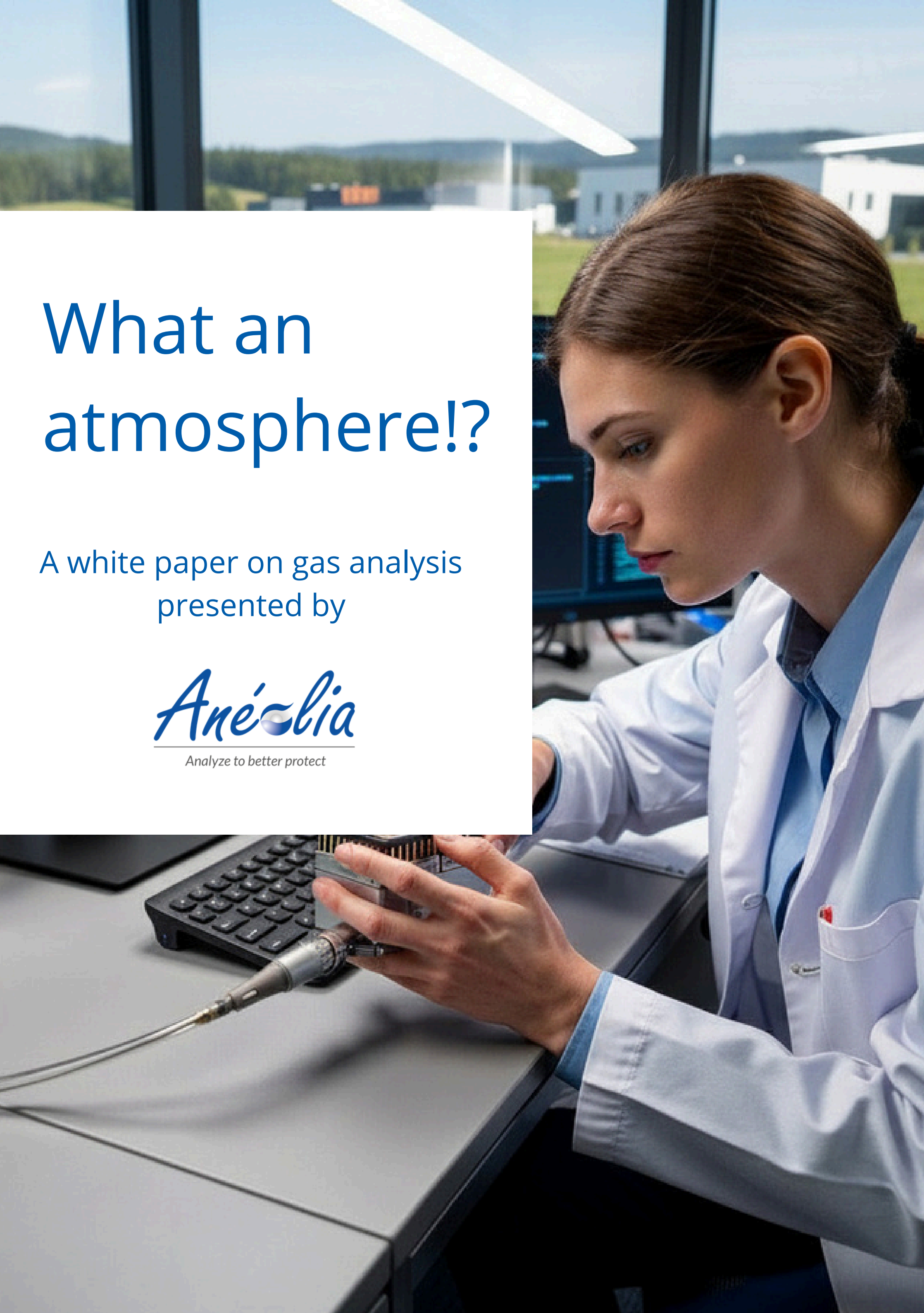


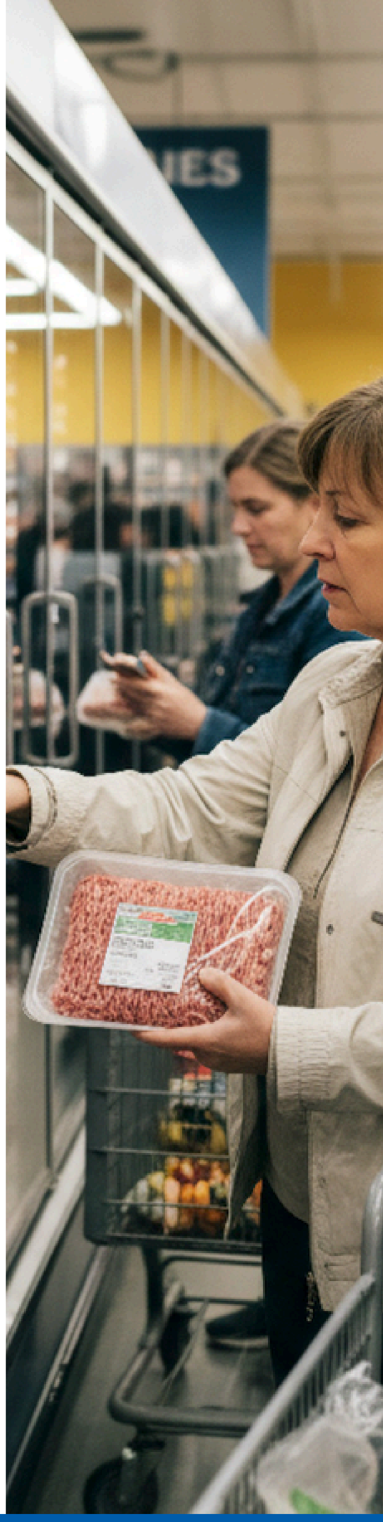
What an atmosphere!?

A white paper on gas analysis presented by

Anéolia

Analyze to better protect

SUMMARY



FOREWORD

After sealing, analyzing the composition of the atmosphere is the second pillar of an effective preservation process; this is the subject of this book. Gas analysis is a vast field with many ramifications. This book will focus primarily on methods commonly used in the packaging industry.

The gases of life

Air is not nothing; it is a substance that is essential to life.

There isn't a child alive who hasn't marveled at the discovery that air isn't nothing, but rather matter, albeit intangible. And yet, this thin shell of gas surrounding the Earth—1 millionth of its mass!—is both the seat and the condition of existence for most living things. Since the advent of photosynthesis in cyanobacteria some 3 billion years ago, leading to the massive production of a particularly reactive molecule, oxygen, and a cheap fuel, sugars, most living organisms began to use this new abundant source of energy: life began to breathe (Figure 1).

This cycle is well known, transforming the Sun's light energy into animal movement in a fascinating biochemical ballet. But this formidable solar energy pump has one drawback: its main intermediary, oxygen, is an unstable molecule—try playing with liquid oxygen! O_2 is toxic to most organisms that existed before photosynthesis, and to a certain extent to those living today. Oxygen's unfortunate tendency to steal electrons from those who possess them starts fires, rusts metals, causes fats to go rancid, degrades polymers, and ages our cells.

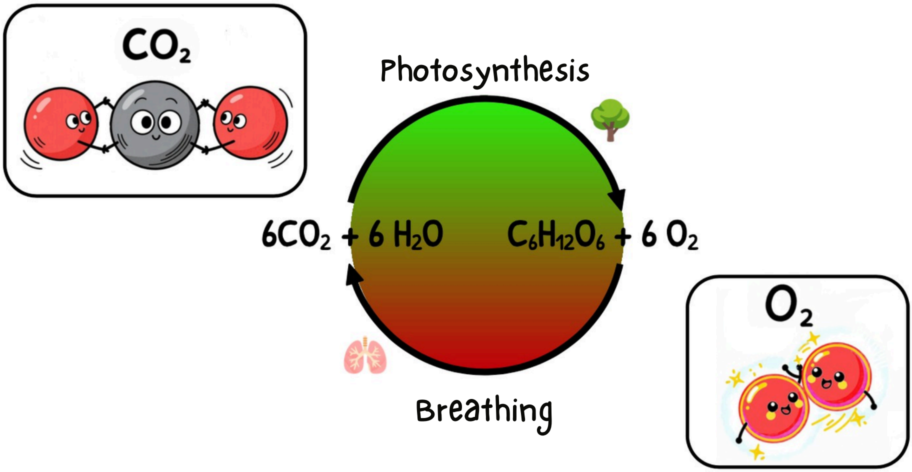


Figure 1. O_2 and CO_2: the gases of life.

While aging is inevitable for everything, everyone would agree that the speed at which this aging occurs makes a clear qualitative difference. The lifespan of a consumer product follows the same logic, and since identical causes lead to similar consequences, the storage environment plays a decisive role in determining the speed at which it ages.

1. Oxygen free radicals produced by respiration are key intermediaries in cellular aging processes.

Character introduction

Air is the protective atmosphere for living organisms. Oxygen, nitrogen, carbon dioxide—these gases drawn from the air also play an essential role in the food and medical sectors, where they too protect living organisms. The focus here is on these gases and a few others commonly found in the packaging industry.

1.2. Oxygen O_2

Role

Omnipresent (21% of the air), essential and yet feared and avoided, oxygen is often the gas analyzed first.

Although oxygen reactivity is sometimes welcome—in respiratory mixtures for resuscitating patients or in trays to preserve the red color of meat—it is more often carefully avoided. Oxygen is commonly excluded from the preservation of oxidation-sensitive goods, whether chemical, pharmaceutical, or food. It is also excluded from many chemical processes, starting with metallurgy.

In the world of packaging, the challenge is often to minimize its presence and ensure that it remains so in the long term.

Optical properties

Oxygen is an apparently colorless gas, but it absorbs light at several wavelengths in the red and near-infrared (liquid oxygen at –183°C is blue). However, the very low absorption at these wavelengths requires sophisticated spectroscopic detection methods (long optical paths, lasers, etc.).
O_2 absorbs strongly between 150 and 200 nm, but the difficulties of implementing spectroscopy in the far UV mean that its detection at these wavelengths is reserved for niche applications.

Magnetic properties

It is a little-known fact that oxygen is a paramagnetic compound. This phenomenon is clearly demonstrated by liquid oxygen, which “sticks” to magnets. Although the effect is weak in the gaseous phase, this remarkable and very specific property enables the use of paramagnetic oxygen sensors.

Chemical properties

– It goes without saying that oxygen is an oxidant. This requires certain precautions when handling it in its pure form, but it also allows it to be detected by various electrochemical methods.

– Due to its magnetism (triplet ground state), oxygen allows certain fluorescent compounds to relax (lose energy) before they emit light, thereby reducing the observed fluorescence. This phenomenon can be used to design fluorescence oxygen sensors.

1.2. Nitrogen N_2

Role

The most abundant element, comprising more than three-quarters of the atmosphere (78%), nitrogen is perhaps also the least accessible for analysis.

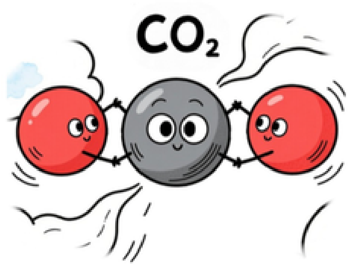
Properties

Chemically very unreactive, transparent across all wavelengths of interest, and lacking any particular electrochemical or magnetic properties, detecting dinitrogen is particularly difficult and requires at least a mass spectrometer. However, in applications requiring diazote, it is not the diazote that matters but the absence of other gases! In practice, there are no diazote sensors, but rather oxygen and/or carbon dioxide sensors and a calculation of the nitrogen level by difference.

1.4. Carbon Dioxide CO_2

Role

Although it accounts for only a tiny fraction of the atmosphere (0.04%), carbon dioxide plays a significant role in plant growth, the greenhouse effect, and the biosphere in general.



In the packaging industry, its most useful property by far is its ability to preserve sterility: when present in sufficient quantities (≥ 20%), CO_2 inhibits microbial growth, thereby significantly extending the shelf life of certain products. Gas analysis also has a safety aspect for people: CO_2 is quickly harmful to humans with an Occupational Exposure Limit Value (OELV source INRS) of 0.5% (it lowers the pH) and risks of asphyxiation that can lead to permanent injury or even death above 4%.

Optical properties

Carbon dioxide is a transparent gas in the visible spectrum, but has very intense absorption bands in the near infrared (which is what makes it a significant greenhouse gas). In fact, non-dispersive infrared (NDIR) sensors are by far the most widely used for measuring CO_2 levels.

Chemical properties

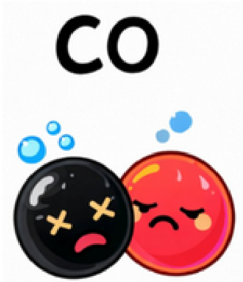
Carbon dioxide dissolves rapidly in basic solutions to form carbonate ions. Using this principle in the vicinity of an electrode equipped with a gas-permeable membrane, the equilibrium between CO_2 gas and carbonate ions in solution can be quantified using electrochemical methods.

1.5. Carbon Monoxide CO

Role

Carbon monoxide is sadly notorious for cases of poisoning, often fatal, resulting from poor combustion in heating systems. By binding to hemoglobin in the blood in place of oxygen, CO is extremely toxic and can cause death within a few hours at concentrations of just 0.1%.

It is this same property that sometimes makes it useful, in very small proportions, in meat packaging, as the carboxymyoglobin formed gives the meat a beautiful bright red color. This practice is common in the United States, Canada, and Australia, but is not permitted in the European Union or Japan.



Optical properties

Like its cousin carbon dioxide, CO has absorption bands in the near infrared, which allows it to be detected using spectrometric sensors.

Chemical properties

The oxidation of CO to CO_2 on the surface of an electrode allows the amount of CO gas to be quantified. This method is the basis for most electrochemical sensors, which are by far the most common type used for CO detection.

1.6. Nitrous oxide N2O

Role

Nitrous oxide is a gas used in medicine for anesthesia, but also in the food industry: it is the propellant gas in whipped cream. Present only in trace amounts in the air, it is mainly of synthetic origin.

Optical properties

Transparent in the visible spectrum, its absorption in the infrared allows it to be detected selectively by NDIR, although the proximity of the CO_2 absorption bands requires the use of narrow optical filters in cases where there is a risk of cross-sensitivity.

1.7. What about the others?

Hydrogen (H_2) has high thermal conductivity and explosive properties, making it relatively easy to detect. Helium (He) and argon (Ar, the third most abundant component of air at 0.9%), both noble gases with low reactivity, often require a mass spectrometer for detection. Ammonia (NH_3), hydrogen sulfide (H_2S), and many others have physical, chemical, and olfactory properties that allow them to be quantified if necessary. Fortunately, this is not often the case in the food packaging or medical sectors.

Expert commentary

Gas is a part of what makes up the universe, a part of us, invisible and everywhere.

In industry, when we talk about gases, we associate them with the risks and dangers they represent, an uncontrollable energy that produces our stars: some can ignite, others explode with the right mixture, another category poisons us, or are foul-smelling and pungent, but so promising sometimes when it comes to tasting cheese!

But we forget those that constantly help us in our daily lives: the breathable ones, the anesthetics, the antiseptic agents, those that enter our amino acid chain, a part of the universe we are made of, but also the sodas we drink!

This book is here to talk about them, about their role that is so accepted and buried that we most often experience them in a breath, in our atmosphere, our atma: in the original sense, breath, essence, soul.
We inhale O_2 and exhale CO_2, the principle of life, breathing. And our foodstuffs decay and ferment, producing other gases, such as C_2H_4 (ethylene from our fruit) and CO_2 from fermentation, among many others.

In several fields, this exchange requires assistance and control. Respiratory assistance, a professional field I come from, to which I am particularly attached and which constantly inspires me, but also controlled or modified atmospheres for better food storage, my second professional life, which I have been practicing for nearly three decades.
It is undoubtedly in the packaging industry that this gas goes completely unnoticed by consumers.

Did you know how fruit always arrives on store shelves looking almost as fresh as when it was picked, even though it has been stored for weeks or months? Or do you think it was picked the day before?

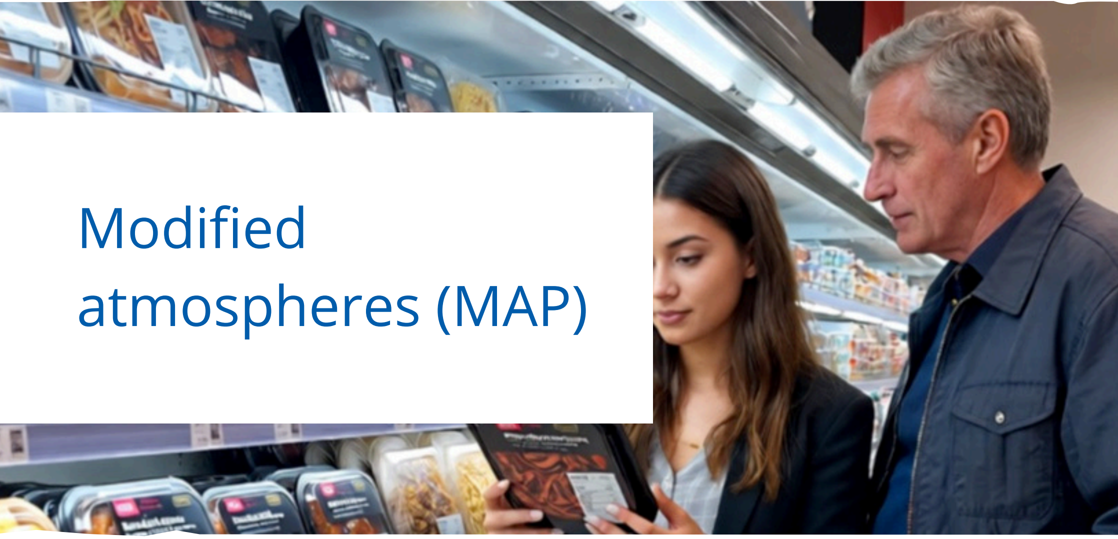
Of course not! But then how is this achieved? Most of the time, we think of refrigeration or freezing. Have you ever tried this with raspberries?
It's difficult to keep them looking good, isn't it?

For raspberries, the atmosphere in their storage area is controlled by inhibiting their metabolism and blocking cellular aging. How? By sending them a massive dose of O_2, more than 80%. Want them to be just the right amount of fresh? Quickly remove the O_2 from the room and send them a small dose of ethylene messenger to wake them up and get them to produce sugar.
Fantastic, isn't it?
But for bananas, you have to avoid ethylene, otherwise they quickly become spotted.

There you have it!
A key principle of human society is knowing how to store food without causing grain silos to explode, preserving the flavors of our food packaging, and limiting microbial and fungal growth. And our friends, the gases O_2, CO_2, N_2, N_2O, and Ar, join in this cycle of life, in this perpetual transformation. They are true allies in food preservation if we know how to control and measure them.

I wish our readers all the best in learning more about how to analyze them, and remember, if we have used them for a purpose, it is so that they remain there, so be careful of leaks!

Eric Schaller, CEO Anéolia



Modified atmospheres (MAP)

Role in food packaging

MAP, or Modified Atmosphere Packaging, involves replacing the air inside packaging with a mixture of gases in order to extend the shelf life of the product while maintaining its quality.

The implementation of MAP packaging requires special attention:
– The packaging material must be impermeable to the diffusion of the gases of interest.
– The packaging must be airtight, or at least have a sufficiently low leakage rate to guarantee the composition of the MAP throughout the product's shelf life (see our first white paper: “Nothing is airtight!”)

In some cases, these gases can be directly incorporated into the product or used to facilitate its packaging, such as carbon dioxide (CO_2) in sparkling drinks or nitrous oxide (N_2O) in whipped cream**.**

Nitrogen N_2

Diazote is used for packaging many products that are affected by the presence of oxygen in the air. This is the case for many sweet and savory snacks, as well as oils, fats, and many chemical and pharmaceutical compounds.

The absence of oxygen prevents oxidation, which causes lipids to become rancid, discoloration (except for red meat), and flavor alteration, thereby significantly increasing the shelf life of many products.

Diazote can be used pure in products that do not present a risk of microbial growth, or mixed with CO_2. In practice, packaging is rinsed with nitrogen to reduce the oxygen content below a limit defined according to the application.

In the case of N_2 packaging, it is therefore not the diazote content that is controlled, but the residual oxygen content.

Carbon Dioxide (CO_2)

CO_2 is used in packaging for its bacteriostatic and fungistatic effect: it completely inhibits microbial growth (bacteria and mold) that can cause food to spoil and deteriorate.

It can be used pure or in combination with nitrogen for products susceptible to oxidation, or in combination with oxygen for meat.

Examples :

Sliced mozzarella packaged in 100% CO_2 can have a shelf life of up to 2 months, compared to only 2 weeks in air.

For pastries stored at room temperature, the standard shelf life increases from 1 week in air to 3 weeks in a 70/30 N_2/CO_2 mixture.

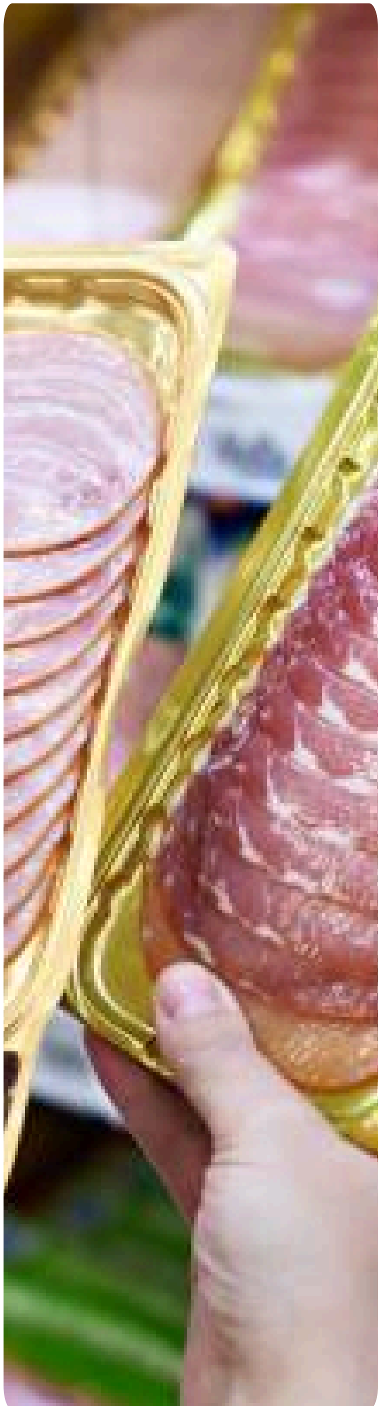
For cream cakes stored at 4°C, the shelf life increases from 3 to 21 days under the same conditions.

Oxygen (O_2)

Oxygen is mainly used for packaging red meat, to which it gives an appetizing bright red color by binding to muscle myoglobin.

It is generally used in combination with carbon dioxide, which acts as a microbial growth inhibitor. Packaging that provides a good barrier to oxygen is required: typically, a polystyrene tray covered and sealed with a 50 µm thick PE/EVOH laminated film, filled with a mixture of O_2/CO_2; 70/30.

While the purely visual effect of oxygen may seem cosmetic compared to the health role of CO_2, it also acts as an indicator. The discoloration of the meat when the oxygen level drops makes it easy to spot defective packaging, which at the same time poses a health risk in the absence of a protective atmosphere.



2.2 Which atmosphere for which product?

The choice of gas mixture (N_2, O_2, CO_2) is specific to the biochemical characteristics of the food in order to maximize its shelf life (best before date) and maintain its organoleptic quality.
For example, switching from a recipe based on animal proteins to one based on vegetable proteins (or a composite product) may require a revision of the MAP mixture. On the other hand, the trend toward offering "clean label" products (with fewer additives and chemical preservatives) dramatically increases dependence on MAP to ensure shelf life and food safety.

The case of CO_2.

When chemical preservatives (such as nitrites, benzoates, or other antimicrobial additives) are removed from a product's recipe, carbon dioxide becomes the main, if not the only, microbial control agent. It then often becomes necessary to increase the CO_2 concentration above 20% to compensate for the loss of the protective effect of chemical preservatives.

Conversely, too high a concentration of CO_2 can have negative effects (impact on taste or sagging of the packaging), which requires precise adjustment and balancing with nitrogen as a filling and stabilizing gas.

– Organoleptic alteration: A slightly acidic or pungent taste can be transferred to the product by dissolved CO_2, particularly in moist products (meat, dairy products).

– Collapse of the packaging: CO_2 is highly soluble in water and fats. If there is too much CO_2, it can dissolve into the product over time, causing the internal pressure to drop and the packaging to collapse.

2.3. Compromised atmosphere: what are the consequences?

A non-compliant gas mixture in modified atmosphere packaging (MAP) has direct and potentially serious consequences for both product quality and consumer safety. These consequences are mainly related to quality issues, due to uncontrolled shelf life (DLC), and health risks in the event of microorganism growth.

DLC Not Compliant

If the O_2 level is too high (packaging under N_2 or N_2/CO_2)

Whether the oxygen content is too high due to a failure to flush the packaging or a leaky package, oxygen will accelerate several degradation mechanisms:

• Color alteration: Browning of certain meats, oxidation of vegetable pigments.

• Rancidity: oxidation of fats, leading to the development of rancid odors and flavors (meat, fish, snacks).

• Loss of nutrients: degradation of vitamins sensitive to oxidation (vitamins A, C, and E). Consumers purchase a product with a specific use-by date, but discover that it has deteriorated before that date, leading to food waste and frustration.

Risk of pathogenic bacteria growth

If the CO_2 level is too low (CO_2 packaging)
The main danger associated with too low a CO_2 level and/or a high residual O_2 content is the potential growth of yeast or bacteria.

This is typically the case with defective packaging, where the gas content gradually exchanges with the surrounding air: the CO_2 level decreases while the oxygen level increases. The leak then becomes a gateway for contamination.

For certain products, the growth of microbes and potentially pathogens such as salmonella, E. coli, or Clostridium botulinum (responsible for botulism) is exponential in the absence of an inhibitor such as CO_2. The health risk becomes real.

Impact on the brand

Rigorous control of the gas mixture is therefore a critical step in the HACCP plan of food manufacturers. It is an essential control point for ensuring product safety and compliance until the use-by date promised to the consumer.

Repeated discoveries of altered products (smell, color) generate complaints, product recalls, and irreversible loss of confidence in the brand and the company's safety standards. A health scandal never happens by chance; it is precisely the role of quality to ensure that it does not happen.

The measure in practice

To ensure the correct composition of a gas mixture, certified and calibrated gas analyzers are used. The accuracy, sensitivity, and selectivity of these analyzers vary depending on the methods employed (electrochemical, optical, etc.), and the choice is made according to the intended application. Modern gas analyzers generally offer very high accuracy, with uncertainties for O_2 and CO_2 of up to 0.1% v/v in absolute value.

3.1. Standards, Units of Measurement, and Tolerances

In general, the composition of a gas is expressed as a volumetric fraction (% v/v, or % volume, which is almost equivalent to mole fractions). It is therefore necessary to distinguish between absolute tolerances, expressed in % v/v, and relative tolerances, expressed as a percentage of the measured value.

In the medical field

The ISO 80601-2-55 standard describes the particular requirements for monitoring respiratory gases.

– For oxygen (O_2) concentration, the tolerance is ±3% v/v (absolute value).

– For carbon dioxide (CO_2), the required accuracy is generally ±0.43% v/v (absolute) + 8% (relative) of the gas concentration.

Example: for a target concentration of 5% v/v, the permissible deviation is approximately ±(0.43 + 0.08 × 5) = ±0.83% v/v.

– For anesthetic agents (N_2O), the deviation must not exceed ±(0.15% v/v (absolute) + 15% (relative) of the gas concentration).

Furthermore, the harmonized and mandatory standard EN ISO 7396-1 specifies requirements for medical gas pipeline systems. It recommends the installation of oxygen and carbon dioxide sensors in rooms where these gases may accumulate, in order to prevent risks related to leaks.

A visual and audible alarm must be triggered if the oxygen level falls below 19.5% or exceeds 23.5%, or if CO_2 exceeds the threshold of 1.5%.

In food packaging

Gas analysis is part of food safety management, generally governed by the standard ISO 22000: Food Safety Management Systems. The standard incorporates Good Hygiene Practices and Good Manufacturing Practices (PRPs), as well as the hazard analysis and critical control points approach (HACCP), and is globally recognized by the Global Food Safety Initiative.

In industrial practice, an acceptable gas composition is one that falls within the tolerance range defined by the quality department for each product.

– Common tolerances: Operators and quality managers generally work with tolerances on the order of 2 to 3% v/v (absolute), or even 5% v/v at the upper end of the scale.
Example: For red meat under MAP (80/20 O_2/CO_2), a measured CO_2 content would be considered acceptable between 17 and 23% v/v, and O_2 up to 75% v/v.

– Fresh products (fruits and vegetables) require low O_2 levels (1 to 5%) and moderate CO_2 levels (2 to 15%). At these low O_2 levels, sensors must provide an absolute accuracy between ±0.1 and ±0.5% v/v in the lower range.

– Tight O_2 tolerances: For products where oxygen must be almost completely absent (dry products, certain plant-based products, ham), the tolerance is much stricter and may require an absolute value below 0.5% or even 0.2%.

3.2. Calibration and Adjustment of Instruments

Some sensor technologies exhibit systematic drift over time, while others may deteriorate suddenly due to exposure to a specific contaminant. To maintain the margin of error within the required range and reduce the risk of biased measurements caused by instrument faults, regular verification of calibration and periodic adjustment of gas sensors are essential.
It is particularly important to follow the manufacturers' recommendations, which may vary considerably depending on the technology and its implementation.

Standards and Definitions

According to the International Vocabulary of Metrology, available in open access:

Calibration of an instrument consists of establishing the relationship between reference values and the indications provided by the instrument (here using certified calibration gases), without modifying the instrument itself.

Adjustment refers to operations such as zeroing, span setting, etc., aimed at correcting the instrument's readings so that they correspond to the reference values. Depending on the instrument and the linearity of its response, adjustment can be performed automatically by the device using measurements at a certain number of points (calibration gases at different concentrations).

Verification is the control operation that confirms whether the metrological performance of the instrument remains within specified tolerances, without altering its settings. After adjustment, verification is necessary to confirm the instrument's compliance; a full recalibration is required only when complete metrological traceability is needed.

Furthermore, the standard ISO 7504:2015 defines all the English-language terms related to gas analysis and calibration. The standards NF ISO 12963 and ISO 6143:2025 describe the calibration methods for instruments and for the calibration gas mixtures themselves, respectively.

A concrete example

Electrochemical O_2 sensors

Let us compare two types of electrochemical oxygen sensors commonly encountered in the packaging industry: galvanic sensors and zirconia sensors (see Section 4.4 for technical details). We will also assume that the sensors are calibrated across the full scale, from 0 to 100% v/v O_2.

Galvanic sensors have an essentially linear response to oxygen concentration, but this response tends to drift over time. A simple adjustment in ambient air is therefore insufficient and may potentially result in a zero offset.

In this case, a rigorous adjustment includes:

– One point using a certified calibration gas at mid-scale, potentially air, but with certified composition. Particular care must be taken to avoid the temptation to use ambient air from production environments, where process gases, humidity, and other aerosols may distort the measurement or even damage the sensor.

– A zero check, typically using pure nitrogen. If necessary, a long purge (45 s) is recommended before performing the adjustment, especially if high accuracy at very low concentrations is required.

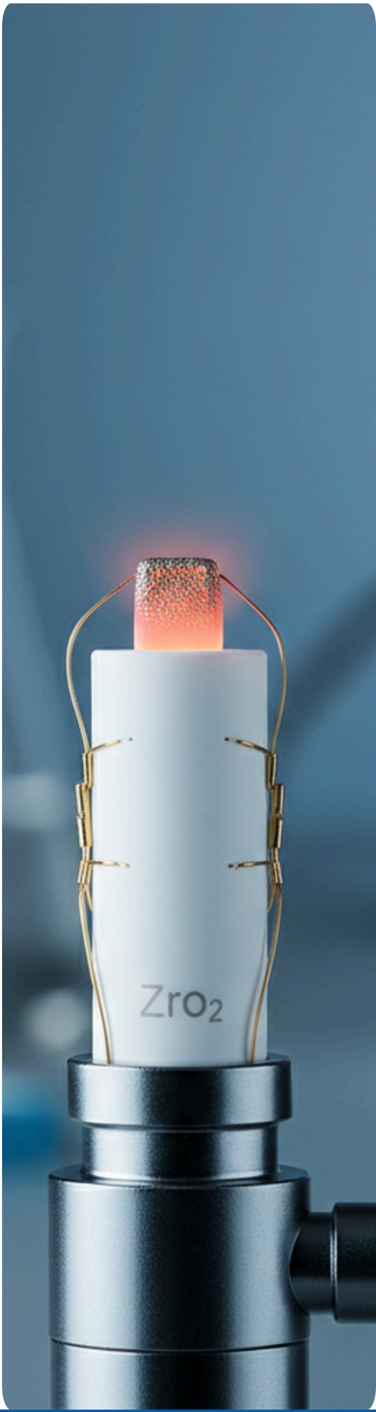
– A verification measurement using a third certified gas mixture.

Zirconia sensors, on the other hand, exhibit less drift under normal operating conditions. However, excessive contamination of the gas being analyzed by water vapor, ethanol, acetic acid, or other substances may require a complete recalibration.

– Since the voltage across a zirconia sensor has a logarithmic dependence on the oxygen concentration, a rigorous calibration across the full measurement range requires up to four measurement points, typically: 100 ppm, 1%, 21% (calibrated air), and 80% v/v O_2.

– Due to the nature of the method, zero measurement is not feasible, as the signal is theoretically infinite and, in practice, does not stabilize.

In all cases, it is essential to perform regular calibration verification measurements using certified gases and to strictly follow the adjustment protocols corresponding to the instruments.



3.3. Production Controls

Gas content is generally monitored at two key stages of the packaging process.

In-line Control
(at the machine inlet)

This control ensures that the gas mixture supplied to the machine is correct (from a gas mixer or ready-to-use premixed gases).

– Equipment: Gas mixer or fixed gas analyzer.
– Function: The gas mixer dynamically adjusts the flow rate of pure gases (nitrogen, oxygen, carbon dioxide) according to the desired percentage to create the MAP atmosphere. It often incorporates sensors to verify the composition before injection into the package.

Quality Control on the Finished Product
(at the end of the line)

This is the most common method used to verify that the gas has been properly injected into the package.
– Equipment: Portable or in-line fixed gas analyzer.
– Principle: The operator withdraws a gas sample from inside the sealed package using a needle and syringe.
– Result: The analyzer displays the composition of the mixture in % v/v of O_2 and CO_2 (and sometimes N_2 by difference).

As with any analysis, sample collection is a step that is just as important as the analysis itself. If performed incorrectly, it can become the primary source of errors and inconsistencies.

Sampling Method

Here we will consider the cases most commonly encountered when monitoring the modified atmosphere (MAP) of a sealed package, whether in production or during product development.

The gas sample is taken using a needle inserted into the package through a septum. The needle is connected to the sensor by tubing, and a pump draws the sample toward the measurement probe. A filter protects the sensor from solid or liquid contaminants (hydrophobic filters are used). Several points must already be checked:

– Proper operation of the pump and leak-tightness of the needle–tubing–instrument assembly (routine instrument maintenance).
– The location and proper sealing of the septum (absolutely avoid placing it on the sealing seams).

– Proper needle positioning: it must completely pierce the upper film of the package but must not touch the product, in order to avoid clogging.

– Filter cleanliness: this is especially important in the case of powdered products (coffee, cocoa), for which a poorly performed previous measurement may have completely clogged the filter.

Sample Volume and Dead Volume

The assembly consisting of the needle, filter, tubing, and measurement cell represents a non-negligible volume of gas that must be purged before the sample can reach the probe.

The volume of gas drawn by the pump — which is a method parameter — must therefore always be significantly greater than this dead volume. Otherwise, the measurement will yield inconsistent results, as it will reflect a mixture of the sample and the gas present in the instrument prior to analysis — often air.

Here again, the importance of a clean filter should not be underestimated, since the pressure losses caused by a partially clogged filter reduce the pump flow rate.

If the pumping time is limited, this may result in an insufficient sample volume and a distorted measurement. Some instruments equipped with a flow meter prevent this type of situation by measuring the amount of gas drawn or by alerting the user to an obstruction in the entire sampling kit.

The choice of instrument and its placement also play a role: the closer the sensor is to the package being analyzed, the shorter the tubing can be and the smaller the dead volume. This can become a determining factor in the case of packages containing small gas volumes and may be critical for operational implementation. Portable devices offer a clear advantage in this respect.

Interference from the Product and Cross-Sensitivities

The tested package contains not only the gas to be analyzed but also a product. This product may not only physically interfere with the measurement — by contaminating the filter or clogging the needle — but may also distort the analysis of the gaseous sample.

Optical methods may exhibit cross-sensitivities with other gases or with aromas and vapors from additives released by the product, as their absorption bands may overlap with the optical filter window. This phenomenon is particularly critical for measurements at low concentrations.

For **electrochemical sensors,** certain contaminants may induce changes in redox potential. Depending on its concentration, carbon dioxide (CO_2) can quickly affect galvanic oxygen detectors, as it is highly soluble in the electrolyte and may precipitate in the form of carbonates.

With a zirconia detector, the sensor temperature allows certain gas mixtures to react, altering their composition. For example, carbon monoxide (CO) reacts with oxygen (O_2) to form carbon dioxide (CO_2) near the electrode, artificially lowering the measured O_2 concentration.

This is the case, for example, with roasted or burnt coffees and other charred products, which tend to release gaseous compounds such as carbon monoxide, as well as more complex organic molecules capable of interfering with measurements. Mustard, like fresh garlic or onions, releases sulfur compounds to which gas sensors are sometimes just as sensitive as our sense of smell.

These organic compounds are, at the very least, detrimental to the membranes and electrode surfaces of electrochemical methods, accelerating their aging and causing calibration drift. Volatile additives in food formulations (ethanol, acetic acid, liquid water in aerosol form) may similarly create interference or even damage the sensors.

Poor Practices

Example 1
The instrument is calibrated in another workshop using a shorter tube than in normal operation. The calibration is validated under these conditions, but in production, with a larger dead volume, the probe is never properly purged by the gas being analyzed.

Example 2
The analysis results are poor; let us check whether the sensor has drifted by comparing it with another instrument on site. Besides the risk of confirming a systematic error if both instruments exhibit the same drift, two analyzers must not be used simultaneously on the same package (risk of competition between the pumps). But if two different products are compared using two analyzers, how can we determine which one is correct?

Example 3
The instrument is tested on a new product and the results appear inconsistent. The instrument is then returned as defective. What is the nature of the product? To what extent is it likely to interfere with the measurement (filter clogging, gas release, specificity of the analytical method)? The instrument may potentially be in good condition, but in its current configuration not suited to the nature of the sample.

Logistics and on-site control

By Franck Cousin, Air Liquide

How is it carried out in a typical installation — from gas mixture production to the end of the packaging line — to ensure the correct gas content and the proper maintenance of the expected proportions?

The methodology for controlling gas composition depends on how the mixture is prepared: industrial premix or on-site mixing.

Supply, Case 1: Ready-to-Use Premixed Gases
This approach is often preferred for small volumes or for users requiring highly precise mixtures.

Step	Practical Process	Quality Control
Source (Supplier)	The gas supplier produces the mixture (ex: N_2 / CO_2 70/30) in bottles or bottle frames, with a high level of precision and traceability.	The supplier is responsible for the certification of the mixture. A certificate of analysis is provided, guaranteeing the composition with documented precision (from 1% to 2%-v/v deviation from the announced value).
Client Site	The gas is conveyed from the bottle to the packaging machine via a pressure reducer and a flow regulator.	Punctual verification of pressure and flow rate. An analysis of the mixture directly at the outlet of the bottle can be carried out to validate the gas before use (less frequent than the analysis on the finished product).

Step	Practical Process	Quality Control
Packaging machine	The mixture is injected directly into the packaging enclosure (or injected via a nozzle).	The mixture is considered correct since certified upstream. The control mainly focuses on sealing and residual O_2 in the finished packaging.

Supply, Case 2: On-Site Gas Mixer
This approach is more common for large volumes or installations requiring frequent changes in gas recipes.

Step	Practical Process	Quality Control
Source	Pure gases (liquid N_2, liquid CO_2, liquid or bottled N_2) are stored in cryogenic tanks or separate bottles.	The client ensures the purity of each gas (supplier certificate).
Gas mixing	Pure gases pass through a dynamic mixer. Precision flowmeters regulate the flow of each gas to achieve the desired ratio (O_2/CO_2, 75/25).	
Packaging machine	The gas mixture is conveyed to the conditioning head.	Control of the injection pressure to ensure efficient air rinsing, or even an online analyzer at the injection point.

End-of-Line Control

Regardless of the supply mode, the final validation of the packaging — and therefore the assurance of proper preservation — takes place at the level of the sealed package.
Method: Headspace analysis. A given volume of the package atmosphere is sampled and analyzed to ensure MAP compliance. This is the final and most important control step.

Objective: Verify that CO_2 and O_2 concentrations comply with specifications.
Sampling (HACCP): It is recommended (ISO 22000) to test samples at fixed intervals (for example every 15 to 30 minutes), depending on the packaging speed or after a machine stop/start.

Ensuring Mixture Preservation (Tightness)

Even once compliance of the package at the end of the line has been confirmed, it must still be maintained throughout the product's shelf life. Preserving the gas mixture in the expected proportions obviously depends on the permeability of the packaging film, but even more critically on the integrity of the film and the quality of the sealing.(3)

Factor	Control Measure	Consequence in case of Default
Permeability of the film	Choice of a film with an adapted Oxygen Transmission (OTR) and water vapor transmission (WVTR) rate	Ensures a sufficiently slow diffusion of the gases of interest through the wall of the packaging
Sealing of welds, tears, micro-leaks	Measurement of the leak flow rate (see DIN55508 for a choice of methods), evaluation of the degree of defect in the packaging.	Loss of MAP and entry of ambient air leading to an uncontrolled DLC and a health risk

(3) we refer the reader to our first work on the subject; "Nothing is watertight!"

Principles and analysis methods

General information

All gas analysis methods are based on measuring a physical-chemical property (spectroscopic, electrochemical, magnetic) whose value depends selectively on the absolute quantity of the compound of interest in the sample. Thus, it is not the volume fraction (% v/v) of the gas relative to the mixture that is measured, but rather its absolute concentration.

In other words, a sample containing 100% oxygen at 210 mbar will give virtually the same measurement results as air at 1000 mbar (where the partial pressure of oxygen is 21% × 1000 mbar = 210 mbar) because both samples contain the same number of oxygen molecules per unit volume: they have the same oxygen density. Although measurements are generally taken at atmospheric pressure, it should be remembered that this varies with the weather (3–4%) and even more so with altitude. Similarly, the temperature of a sample influences its density and therefore the measurement result. In practice, for the same sample, a variation in temperature of 10°C or in pressure of 30 mbar changes the measurement result by approximately 3% (relative).

Some instruments correct for this variation by taking pressure and temperature conditions into account, or even by measuring them. In all cases, regular calibration in accordance with the manufacturer's recommendations and applicable standards is essential to obtain valid results.

Optical sensors using absorption spectrometry

Far beyond gas analysis, quantifying a substance by measuring its ability to absorb light at a specific wavelength is a standard method in chemical analysis. The principle is simple: the absorbance (4) of a light beam is proportional to the concentration of chromophore—the compound of interest absorbing light at the wavelength studied—multiplied by the length of its path through the sample (the optical path). The thicker the sample, the more opaque it is; this is Beer-Lambert's law.

Non-dispersive infrared (NDIR) sensors

The vast majority of industrial gases are transparent in the visible spectrum and only absorb in the ultraviolet (UV) or infrared (IR) spectrum. IR sensors are widely used because all polyatomic gases have absorption bands in this range. Rare gases such as helium and argon are completely transparent in IR.

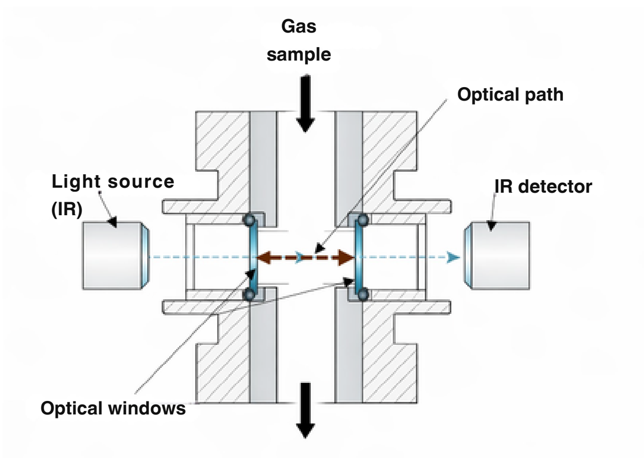


Figure 2. General diagram of an NDIR sensor

(4) Absorbance, A, is the logarithm of the ratio of the light intensity measured after passing through the sample (I) to the intensity emitted upstream (I0): A = –ln (I/I0). Beer-Lambert's law relates this measurement to the concentration of the chemical species, c (in mol·L–1): A = ε·l·c, where ε is the molar absorption coefficient (in L·mol–1·cm–1) and l is the optical path length (in cm).

In theory, this makes it possible to create sensors for most gases of interest, provided that the specific wavelength can be emitted and detected, and that the optical path is long enough for the absorption to be detectable. In practice, a broad-spectrum IR source is often used, and the detector is equipped with an optical filter that transmits only through a narrow window around the selected wavelength. A second channel, equipped with a second filter centered on a wavelength for which the sample is transparent, serves as a reference. By multiplying the channels, a single sensor can be used to quantify different gases.

NDIR sensors are particularly used for CO_2 measurement, whether full-scale or trace measurement (only the length of the optical path varies). Carbon dioxide (CO_2) has a very intense absorption band at 4.26 μm, which is by far the most commonly used for NDIR sensors. Some applications rely on a less intense absorption band at 2.7 μm.

Carbon monoxide (CO) can also be quantified using this method between 4.60 and 4.67 μm, as can nitrous oxide (N_2O) at around 4.50 μm.

Methane and saturated hydrocarbons in general can be detected, albeit non-selectively, between 3.38 and 3.45 μm.

Tunable Diode Laser Absorption Spectroscopy (TDLAS)

Oxygen has a weak absorption band in the infrared at the limit of the visible spectrum (760 nm, hence the slightly bluish color of liquid oxygen). The low intensity of this band complicates the use of NDIR sensors, requiring long optical paths to obtain sufficient absorbance. Technologies based on laser diodes as a light source (TDLAS) are much more sensitive and, above all, extremely selective in wavelength, with a bandwidth of 20-30 fm (10–13 – 10–14 m) and a certain range of modulation around the central wavelength.

By choosing the diode and therefore the wavelength, the method can be applied to many compounds (H_2, H_2S, NH_3, SO_2, etc.). However, its most widespread use is for detecting oxygen in complex gas mixtures, particularly in chemical processes, in order to prevent the formation of explosive atmospheres.

In the packaging sector, applications rarely require this degree of selectivity. Less expensive electrochemical methods are therefore often preferred. However, new TDLAS methods, which are potentially non-destructive for packaging, have recently emerged.

UV-Visible Spectrometry

Of little use in the packaging sector, spectrometry in the visible or near-UV range is used in industry to detect ozone (O_3), sulfur dioxide (SO_2), dichlorine (Cl_2), and nitrogen oxides (NO, NO_2).

Fluorescence quenching sensors

Fluorescence is a fundamental process in which a compound re-emits light at a specific wavelength after absorbing light at a wavelength that is lower than or equal to that wavelength. Oxygen has the particular property of interfering with fluorescent compounds by inhibiting their light emission.

Sensors based on this method require a light source focused on the fluorescent compound contained in the probe, and a detector specific to the wavelength of the fluorescence. In the absence of oxygen in the sample, fluorescence is at its maximum, and decreases with increasing oxygen concentration (according to the Stern-Volmer equation).

Highly sensitive, even at low concentrations, selective, and with short analysis times, this method is nevertheless sensitive to conditions (temperature, pH, source stability, and optical alignment) and is more expensive than electrochemical probes.

Electrochemical sensors

Galvanic sensors

Galvanic sensors are based on the principle of the battery. In a battery, electrons are transferred from a reducing agent to an oxidizing agent by circulating in a conductive circuit. The charge balance is achieved through an electrolyte, often an aqueous solution, between the two electrodes. In the case of a galvanic detector, it is the compound to be analyzed that acts as the reducing agent or oxidizing agent, with the electric current generated by the battery quantifying the presence of the compound.

The method can be applied to other gases, but oxygen sensors are by far the most common. Oxygen is then the oxidizing agent, diffusing through a permeable membrane to recover electrons at the cathode. A lead anode separated by a liquid electrolyte transfers its electrons to the circuit (Figure 3).

These sensors generally suffer from output signal drift over time due to electrode wear, which varies in speed depending on conditions of use. However, by performing regular adjustments (see Section 3.4), their accuracy remains entirely satisfactory. Their longer response time (≈ 750 ms) compared to zirconia sensors (≈ 150 ms) is compensated for by a much higher tolerated gas flow rate, bringing the complete analysis to a comparable duration.
For oxygen measurement, galvanic sensors often represent an attractive compromise between cost and performance. For oxygen measurement, galvanic sensors therefore often represent an attractive compromise between cost and performance.

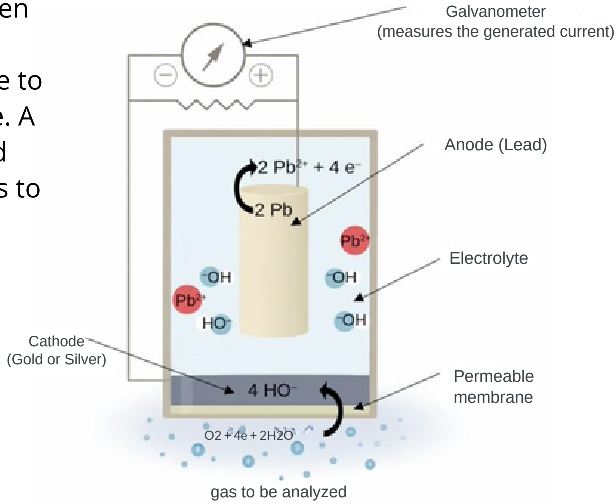


Figure 3. Diagram of a galvanic oxygen sensor

Solid zirconia electrolyte (O_2)

The zirconia oxygen sensor operates on the basis of an electrochemical equilibrium between oxygen gas and oxide ions (O_2–) that can diffuse rapidly through zirconia (ZrO_2) ceramic heated to between 300 and 600°C. This reaction occurs on one side of the detector with a reference gas (typically air) and on the other side with the sample.

If the sample and the reference gas do not have the same oxygen concentrations, the difference in redox equilibrium on either side of the electrolyte leads to the creation of a potential difference between the two permeable electrodes located on each side of the electrolyte.

Slightly more expensive than galvanic sensors, zirconia sensors offer good durability, reliability, accuracy, and fast response times. They are used in the packaging industry, but also in the automotive industry (lambda probes) to control combustion by analyzing the oxygen in exhaust gases.

However, there are some limitations:
– Long start-up time (10 min) to bring the probe up to temperature. – Limited gas flow rate to prevent excessive cooling of the probe
– The device cannot be moved while in operation due to the risk of breaking the zirconia ceramic, which is particularly fragile at high temperatures (not well suited to portable applications).
– The sensitivity of the zirconia ceramic surface to potential pollutants.

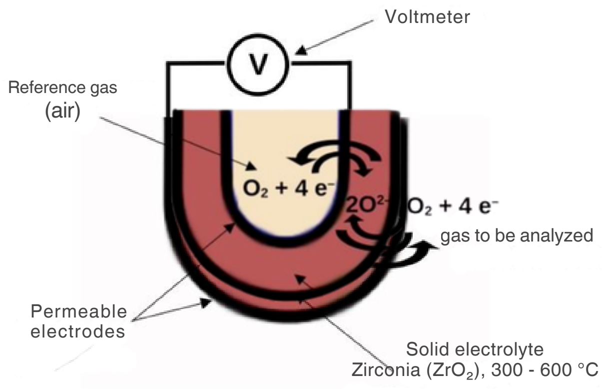


Figure 4. Diagram of a zirconia oxygen sensor

Paramagnetic sensors (O_2)

In its fundamental state, oxygen (O_2) is a paramagnetic molecule, which gives it significant magnetic susceptibility: it “sticks” to magnets, like iron or nickel. While liquid oxygen (-183°C) does indeed stick to a good magnet, it should be noted that thermal agitation in the gas phase makes the phenomenon less intense—there is no magnet strong enough to separate oxygen from air, or even enrich it significantly!

This remarkable property of oxygen makes the method extremely selective. Among “common” gases, only nitrogen oxides (NO and NO_2) have the same property, albeit to a lesser extent, and they are only ever present in very low concentrations.

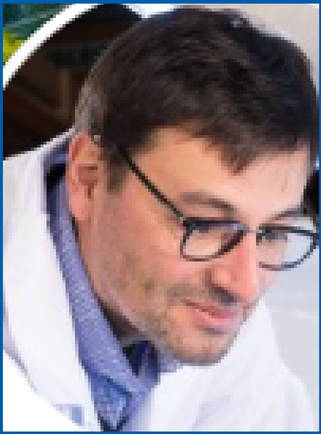
In the probe, the sample and an auxiliary gas—usually N_2—flow through a cavity with a suitable geometry in the presence of a magnetic field. The difference in flow between the two gases depends on the oxygen composition of the sample and can be measured using a mass flow meter, for example.

Thermal conductivity sensors

Thermal conductivity sensors rely on differences in the heat-conducting capacity of gases. Very useful for detecting dihydrogen (H_2) or helium (He), the slight differences in conductivity between oxygen and nitrogen (and to a lesser extent carbon dioxide) make the method less selective and therefore unsuitable for packaging applications.

Safety

By Franck Cousin, Air Liquide



Risk of asphyxiation (anoxia)

This is the most serious risk in the event of a leak in a confined space, mainly linked to the use of nitrogen and carbon dioxide.

– N_2 Nitrogen, the main component of air, is an inert but non-toxic gas. However, a significant nitrogen leak in a poorly ventilated area can displace oxygen from the ambient air. If the oxygen concentration falls below 19.5% (with a critical threshold below 16%), the operator will suffer from anoxia (lack of oxygen). Insidious because it is often odorless and without immediate warning signs, it can lead to fainting and death.

– CO_2 Carbon dioxide is heavier than air and tends to accumulate on the ground. In addition to displacing oxygen (risk of asphyxiation), high concentrations of CO_2 (above the OEL, for example 0.5% or 5000 ppm over 8 hours) can have direct physiological effects (increased heart and respiratory rates, lowered blood pH, headaches, cognitive impairment) that can lead to death at concentrations above 4%.

Risks associated with oxygen

The main risks associated with oxygen are fire and explosion. Air, which naturally contains 21% oxygen, is already conducive to combustion. Even a slight enrichment in oxygen significantly increases the risks and intensity of combustion reactions, making fires more likely and more difficult to control.
In its liquid form, oxygen is a particularly aggressive and potentially explosive substance that must be handled with extreme caution.

Cryogenic risks (cold burns)

In liquid form (cryogenic), gases such as liquid nitrogen have extremely low temperatures (liquid nitrogen boils at –196°C at atmospheric pressure). Direct contact of the skin or eyes with liquid gas, uninsulated pipes, or splashes of cryogenic products can cause severe burns.

Pressure-related risks

All gases used in MAP processes are stored and transported to the machines under high pressure (in cylinders, frames, or tanks).
– Rupture/Leakage. Poorly maintained or damaged installations (pipes, fittings) can cause leaks, ruptures, or even material projections under pressure.
– Overpressure: The vaporization of a liquid gas causes a very large increase in volume (1 liter of liquid nitrogen produces approximately 700 liters of gas), which can cause overpressure and explosions in unsuitable equipment (tanks, pipes).

Safety measures

– Effective ventilation: ensure sufficient air renewal and mechanical ventilation of production areas.
– Gas detectors: oxygen and/or carbon dioxide detectors equipped with audible and visual alarms must be installed in the relevant work environments. These devices are the primary and most reliable means of preventing the risks of asphyxiation (N_2 and CO_2) or fire (O_2), and must also be regularly checked and calibrated to ensure compliance with safety protocols.
– Personal Protective Equipment (PPE): cryogenic gloves, protective goggles, and appropriate clothing are required for any work on cryogenic equipment.
– Training: As in any technical field, a thorough understanding of potential risks, as well as their causes and consequences, is key to effective risk management. Training operators on the specific risks of gases (asphyxiation, pressure, cold) and on emergency procedures is essential in this area.

Conclusion

Whether it's the risk of accidents at the production site, health risks related to packaging quality, or economic risks associated with damage to the company's image, prevention is based on a clear logic: measure, analyze, decide.

Having reliable data is a prerequisite for rigorous analysis of the operation and risks associated with an industrial process. In the packaging sector, gas analysis and leak measurement precisely address this fundamental metrological challenge. But measurement data alone is not enough: it must also be interpreted in the context of product requirements.

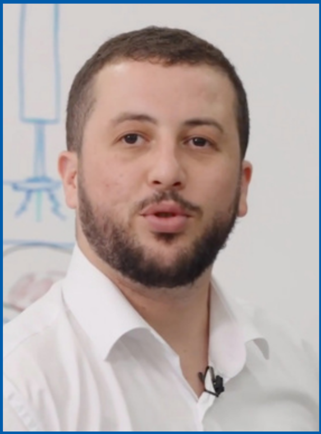
What tolerance is acceptable for the composition of a MAP? What is the maximum leak size for a given type of packaging? What impact do these parameters have on product compliance and safety in the short and long term?

With automated mass production, these issues take on an essentially statistical nature: beyond compliance with a threshold value, it is the distribution of measured values and their evolution over time that become key performance indicators (KPIs) for production. The analysis of packaging compliance and its internal atmosphere is therefore not limited to identifying deviations, but also allows for the definition of objectives that are truly specific, measurable, achievable, realistic, and time-bound (SMART).

In this context, staff training—from production to management—is a key lever. Qualified teams equipped with appropriate measurement and analysis tools are able to translate production data into targeted operational decisions at each stage of the process. When properly integrated with industrial objectives, gas analysis combined with leak measurement becomes a valuable tool for controlling and optimizing production.

Developing the collection and intelligent use of solid data is no longer a matter of industrial orientation. It is the rational response to the increasingly pressing economic and societal imperatives of process safety, product reliability, and accident prevention, both material and human.

Expert commentary



When we talk about gas analysis, we often talk about percentages, sensors, and tolerances.
But ultimately, what we are really talking about is protection.

Protecting a product means protecting those who consume it.
It means protecting the manufacturer, whose reputation and image are at stake.
It means protecting trust.
And, beyond that, it means protecting our own families and children, because we ourselves are consumers of what the industry produces.

Analyzing an atmosphere is not simply measuring the concentration of O_2 or CO_2.
It is seeking to understand an invisible balance.
It is accepting that behind seemingly simple packaging lies a living, dynamic, and sometimes fragile system.

We measure in order to understand.
We understand in order to anticipate.

And we anticipate in order to avoid accidents, deviations, and poor quality.
Technology only makes sense if it serves this mission.
A precise sensor, a reliable measurement, a rigorous protocol: none of these are ends in themselves.
They are tools for reducing uncertainty, informing decisions, and making processes safer and more responsible.

In a context where formulations are evolving, with fewer additives and stricter health requirements, gas analysis is becoming a discreet but essential pillar of food and industrial safety.

Our commitment is simple:
to continue developing robust, understandable, and reliable solutions,
to support our partners in mastering their processes,
and to make measurement not a constraint, but a lever of trust.

Because ultimately, behind every measurement taken and every decision made, there is a consumer or a patient, with an impact on their lives.

And that's why we analyze.

Lyes Irid, Technical Director at Anéolia

Anéolia

Analyze to better protect

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