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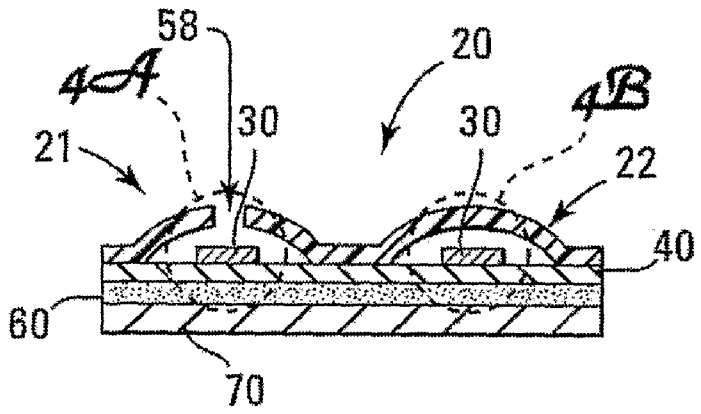


Fig. 3

(57) Abstract: A self-contained, remotely interrogatable, autonomously positionable, pressure probe (20) set from which the volume fraction of a gaseous target-analyte (V_A) in a mass, susceptible to changes in both total pressure of the mass (P_T) and concentration of target-analyte in the mass (V_A), can be ascertained, and methods of manufacturing and using. The probe set includes (i) a first probe (21) comprises an optically-active, target-analyte partial pressure sensitive material (31) configured and arranged to experience changes in P_A in the mass, whereby the first probe can report P_A in the mass, and (ii) a second probe (22) comprises an optically-active, P_A- sensitive material constrained to experience changes in P_T without experiencing changes in the V_A, whereby the second probe can report P_T of the mass.

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PHOTOLUMINESCENT ANALYTE PARTIAL VOLUME PROBE SET

BACKGROUND

[0001] Solid-state polymeric materials based on oxygen-sensitive photoluminescent dyes are widely used as optical oxygen sensors and probes. See, for example United States Published Patent Applications 2009/0029402, 2008/8242870, 2008/215254, 2008/199360, 2008/190172, 2008/148817, 2008/146460, 2008/117418, 2008/0051646, and 2006/0002822, and United States Patents 7,569,395, 7,534,615, 7,368,153, 7,138,270, 6,689,438, 5,718,842, 4,810,655, and 4,476,870. Such optical sensors are available from a number of suppliers, including Presens Precision Sensing, GmbH of Regensburg, Germany, Oxysense of Dallas, Texas, United States, and Luxcel Biosciences, Ltd of Cork, Ireland.

[0002] Such oxygen-sensitive photoluminescent dyes respond to the partial pressure of oxygen (P_{O2}), and are widely used in pressure-sensitive paints that can be applied to the surface of an object and interrogated to determine pressure distribution on the surface of the object exposed to a gas of known composition. See, for example United States Published Patent Applications 2007/112166, 2007/105235, 2006/101906, 2005/288475, 2004/0249593, 2004/091695, and 2003/175511, and United States Patents 7,290,444, 7,176,272, 7,127,950, 5,965,642, 5,854,682, 5,818,057, 5,612,492, 5,359,887, 5,341,676, 5,307,675, and 5,186,046.

[0003] Manufacturers and suppliers of labile products, such as medical and biological products, pharmaceuticals and foodstuffs, typically package such products in a hermetically sealed package that has been flushed with an inert gas, such as nitrogen or a mixture of nitrogen and carbon dioxide, for purposes of reducing the concentration of oxygen within the package and thereby increasing the shelf-life of the product. It is known to employ oxygen sensitive optical probes within such packaging for providing a quick, easy, reliable and non-destructive means for measuring the concentration of oxygen within the packaging, from which the manufacturer can evaluate the integrity of the packaging process and/or the shelf-life status of packaged product in inventory. See, for example United States Published Patent Application 2009/0028756.

[0004] Such probes can accurately and reliably measure the content (volume fraction or percentage) of oxygen within packaging only when the total pressure within the packaging is known and remains substantially constant. However, in situations where a package is subject to appreciable fluctuations in total pressure within the package, such probes cannot consistently and reliably provide an accurate measurement of oxygen content as the probes are co-sensitive to changes in both oxygen content and total pressure.

[0005] Hence, a substantial need exists for a quick, easy, reliable and non-destructive means for consistently and reliably measuring oxygen content (volume fraction or percentage) within a hermetically sealed packaging susceptible to both changes in oxygen concentration and changes in total pressure.

SUMMARY OF THE INVENTION

[0006] A first aspect of the invention is a probe set from which the volume fraction of a gaseous target-analyte (V_A) in a mass, susceptible to changes in both total pressure of the mass (P_T) and partial pressure of target-analyte in the mass (P_A), can be ascertained. The probe set includes a first probe and a second probe. The first probe comprises an optically-active, target-analyte partial pressure (P_A) sensitive material configured and arranged to experience changes in P_A in the mass, whereby the first probe can report P_A in the mass. The second probe comprises an optically-active, target-analyte partial pressure sensitive material constrained to experience changes in P_T without experiencing changes in the V_A, whereby the second probe can report P_T of the mass. Working together the probes form a probe set capable of providing an accurate determination of V_A in a mass.

[0007] The second probe is preferably a self-contained, remotely interrogatable, pressure probe including at least (i) a hermetically sealed, flexible, gas impermeable sachet capable of equilibriating to a surrounding pressure, (ii) an optically-active, target-analyte partial pressure sensitive material within the sachet, and (iii) a gaseous headspace within the sachet containing a known volume fraction of the target-analyte (V_A^0). The sachet is preferably made of a material with a very low gas permeability, most preferably a material that is gas impermeable, so as to prevent any meaningful change in the composition of the gas within the headspace of the sachet over the intended lifespan of the probe set.

[0008] A second aspect of the invention is an article of commerce comprising (i) a product retained within a hermetically sealed chamber of a package, and (ii) a probe set according to claim 1 within the chamber operable for sensing and reporting total pressure and target-analyte partial pressure within the chamber.

[0009] A third aspect of the invention is a method for determining the volume fraction of a target-analyte (V_A) within a hermetically sealed package employing a pressure probe set according to the first aspect of the invention. The method includes the steps of (A) obtaining an article of commerce according to the second aspect of the invention, (B) obtaining at least one analytical instrument capable of reading the optical activity of the first and second probes, (C) taking a reading from the first probe with an obtained analytical instrument, (D) correlating the value of the reading to a target-analyte partial pressure value (P_A) of the hermetically sealed chamber, (E) taking a reading from the second probe with an obtained analytical instrument, (F) correlating the value of the reading to a total pressure value (P_T) of the hermetically sealed chamber, (G) calculating V_A within the chamber of the package from the values of P_T and P_A, and (H) reporting the calculated V_A within the chamber of the package.

[0010] The first and second probes are preferably constructed so that they may both be read with a single analytical instrument.

[0011] A fourth aspect of the invention is a method of manufacturing a probe set according to the first aspect of the invention. The method includes the steps of (A) preparing a composition of a target-analyte partial pressure sensitive photoluminescent dye in a suitable carrier matrix, (B) applying the composition to a first support material, creating a first optically active target-analyte partial pressure sensitive sensor effective as the first partial pressure probe, (C) applying the composition to a second support material creating a second optically active target-analyte partial pressure sensitive sensor, and (D) hermetically sealing the second sensor and a gas having a known volume fraction of target-analyte (V_A^0) within a flexible, gas impermeable sachet to form the second total pressure probe.

[0012] A preferred method of manufacturing the probe sets includes the steps of (1) hermetically packaging optically-active, target-analyte partial pressure sensitive material in a

gaseous headspace having a known volume fraction of target-analyte (V_A^0) within flexible, gas impermeable pockets on a blister pack, and (2) perforating the blister pack so as to expose selective pockets to the surrounding environment and form pairs of adjacent perforated and unperforated pockets on the blister pack, whereby the perforated pockets are first probes and the unperforated pockets are second probes.

[0013] The blister packs preferably have one column of perforated pockets, one column of unperforated pockets and a plurality of rows with a line of weakness between each row.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014] Figure 1 is a top view of one embodiment of the probe set aspect of this invention provided as a continuous roll of probe sets.

[0015] Figure 2 is a top view of a leading portion of the continuous roll of probe sets depicted in Figure 1.

[0016] Figure 3 is an enlarged cross-sectional end-view of the probe set depicted in Figure 2 taken along line 3-3.

[0017] Figure 4A is a grossly enlarged cross-sectional end view of the first probe depicted in Figure 3.

[0018] Figure 4B is a grossly enlarged cross-sectional end view of the second probe depicted in Figure 3.

[0019] Figure 5 is a side view of one embodiment of a hermetically sealed bottle containing a carbonated beverage and one of the probe sets depicted in Figures 1 and 2 with the probe set being interrogated by an analytical instrument.

[0020] Figure 6 is top view of the bottle depicted in Figure 5.

[0021] Figure 7 is a side view of one embodiment of a hermetically sealed container containing a labile food product and one of the probe sets depicted in Figures 1 and 2.

DETAILED DESCRIPTION OF A PREFERRED EMBODIMENT

Definitions

[0022] As used herein, including the claims, the phrase "***gas impermeable***" means a gas transmission rate of less than 30 c^3/m^2 day when measured in accordance with ASTM D1434.

[0023] As used herein, including the claims, the term "***target-analyte***" refers to a gaseous chemical substance, typically O_2, or CO_2, capable of modulating the optical signal emanating from an optically-active material such as a photoluminescent dye. The modulating effect may be achieved by quenching, (de)protonation or other means.

Nomenclature

10	Probe Array
$10_{Column\ 1}$	First Column of Probes in Probe Array
$10_{Column\ 2}$	Second Column of Probes in Probe Array
10_{Row}	Row of Probes in Probe Array
19	Line of Weakness Between Rows
20	Probe Set
21	First Probe
21i	First Probe Indicia
22	Second Probe
22i	Second Probe Indicia
30	Solid State Composition
31	Target-Analyte-Sensitive Photoluminescent Dye
32	Target-Analyte-Permeable Polymer Matrix
40	Support Layer or Lidding
50	Formable Web

57 Pockets in Formable Web

58 Opening Into Second Probe Pockets

59 Cavity defined by Pockets

60 Pressure Sensitive Adhesive Layer

70 Release Liner

80 Outer Packaging for Roll of Probe Sets

100 Packaging or Container

101 Transparent or Translucent Cap or Covering on Package

108 Headspace within the Packaging

109 Retention Chamber of Packaging

200 Analytical Instrument

A Target-Analyte

P Product

$\mathbf{P_A}$ Partial Pressure of an Analyte

$\mathbf{P_T}$ Total Pressure of a Mass

$\mathbf{V_A}$ Volume Fraction of an Analyte in a Confined Space (*e.g.*, the Retention Chamber of Packaging)

$\mathbf{V_A^0}$ Known Volume Fraction of an Analyte in a Confined Space (*e.g.*, the Headspace of the Cavity defined by the Pockets)

Description

Theory

[0024] The present invention utilizes the sensitivity of photoluminescent dyes to the partial pressure of an analyte (P_A) and Dalton's Law of Partial Pressure to provide a probe set capable of noninvasively measuring the partial pressure of an analyte (P_A) and the total pressure (P_T) of a sample susceptible to changes in both total pressure and concentration of analyte, from which the partial volume of the analyte (V_A) and thereby the concentration of the analyte ($\%_A$) in the sample can be calculated.

Measuring Partial Pressure of an Analyte (P_A)

[0025] The methods and compositions described herein are based on the quenching of photoluminescence by an analyte, typically oxygen (O_2). Luminescence encompasses both fluorescence and phosphorescence. Electromagnetic radiation in the ultraviolet or visible region is used to excite molecules to higher electronic energy levels. The excited molecules lose their excess energy by one of several methods. One of those methods is fluorescence. Fluorescence refers to the radiative transition of electrons from the first excited singlet state to the singlet ground state (S_1 .to S_0). The lifetime of fluorescence is relatively short, approximately 10^{-9} to 10^{-7} seconds. However, intersystem crossing from the lowest excited singlet state to the triplet state often occurs and is attributed to the crossing of the potential energy curves of the two states. The triplet state so produced may return to the ground state by a radiative process known as phosphorescence. Phosphorescence is the radiative relaxation of an electron from the lowest excited triplet state to the singlet ground state (T_1 to S_0). Because the transition that leads to phosphorescence involves a change in spin multiplicity, it has a low probability and hence a relatively long lifetime of 10^{-4} to 10 seconds. Fluorescent and phosphorescent lifetime is known to change in a defined fashion relative to changes in P_A capable of quenching the photoluminescent molecules. Hence, the P_A in fluid communication with a photoluminescent material can be determined by measuring photoluminescence lifetime.

Measuring Total Pressure (P_T)

[0026] Dalton's Law of Partial Pressure establishes that the total pressure (P_T) of an ideal gaseous mixture is equal to the sum of the partial pressures of the individual constituent gases (P_n). This law is represented mathematically for a two constituent mixture as:

$$P_T = P_A + P_B$$

[0027] A corollary to Dalton's Law of Partial Pressure establishes that a percentage change in the total pressure of a compositionally static gaseous mixture results in an identical percentage change in the partial pressure of each constituent gas. This corollary law is represented mathematically for a two constituent mixture as:

$$(\Delta P_T)/(P_{T\,Start}) = (\Delta P_A)/(P_{A\,Start}) = (\Delta P_B)/(P_{B\,Start})$$

Wherein $\Delta P = P_{New} - P_{Start}$

[0028] Application of these laws permits the total pressure (P_T) of a compositionally static gaseous mixture to be calculated from a determination of the partial pressure of a given constituent of that gaseous mixture (P_A) so long as at least one pair of correlated values for total pressure (P_T) and partial pressure (P_A) of that constituent gas are known. For example, a gaseous mixture of 79% N_2 and 21% O_2 (*i.e.*, air) at a total pressure (P_{Air}) of 1 atmosphere (101.325 kPa) is known to have a nitrogen partial pressure P_{N2} of 0.79 atmospheres (80.047 kPa) and an oxygen partial pressure P_{O2} of 0.21 atmospheres (21.278 kPa). If a subsequent analysis of this gaseous mixture indicates that the P_{O2} has increased from 21.278 kPa to 30.000 kPa, the total pressure of the air (P_{Air}), assuming no change in the composition of the air, can be calculated as follows:

$$\Delta P_{O2} = 30.000 \text{ kPa} - 21.278 \text{ kPa} = 8.722 \text{ kPa}$$

$$(\Delta P_{O2})/(P_{O2\ Start}) = 8.722 \text{ kPa} / 21.278 \text{ kPa} = 0.410$$

$$(\Delta P_T)/(P_{T\ Start}) = 0.410$$

$$(P_{T\ New} - P_{T\ Start})/(P_{T\ Start}) = 0.410$$

$$(P_{T\ New} - 101.325 \text{ kPa})/(101.325 \text{ kPa}) = 0.410$$

$$P_{T\ New} = 142.868 \text{ kPa}$$

[0029] Hence, total pressure (P_T) can be determined by measuring the photoluminescence lifetime of a target-analyte sensitive photoluminescent material exposed to a gaseous mixture that is capable of dynamically equilibrating to the surrounding pressure but has a known and static concentration of the target-analyte (P_A).

Calculating Volume Fraction of an Analyte (V_A)

[0030] The volume fraction of an analyte (V_A) in a sample, and thereby the concentration of the analyte ($\%_A$) in a sample, can be calculated from the analyte partial pressure (P_A) in the sample and the total pressure (P_T) of the sample using the following equations:

$$V_A = (P_A / P_T)$$

$$\%_A = (V_A)(100)$$

[0031] Hence, V_A, and thereby $\%_A$, in a sample can be accurately ascertained by measuring P_A in the sample and P_T of the sample.

[0032] Applicant has discovered an inexpensive, self-contained, remotely interrogatable and autonomously positionable probe set **20** capable of quickly, easily and reliably ascertaining and reporting both P_A and P_T of a sample susceptible to both changes in oxygen concentration and changes in total pressure, such as the headspace **108** of a filled beverage bottle **100** or the headspace **108** of a filled retort package **100**, in a non-invasive and non-destructive manner.

Construction

[0033] A first aspect of the invention is a probe set **20** from which the volume fraction of a gaseous target-analyte **A** in a mass (V_A), susceptible to changes in both total pressure of the mass (P_T) and partial pressure of target-analyte **A** in the mass (P_A), can be ascertained. The probe set **20** includes a first probe **21** capable of detecting P_A and a second probe **22** capable of detecting P_T. The first probe **21** comprises an optically-active, target-analyte partial pressure sensitive material **30** configured and arranged to experience changes in target-analyte partial pressure P_A in the mass, whereby the first probe **21** can report P_A in the mass. The second probe **22** comprises an optically-active, target-analyte partial pressure sensitive material **30** constrained to experience changes in P_T of the mass without experiencing changes in the V_A in the mass, whereby the second probe **22** can report P_T of the mass.

[0034] For purposes of simplicity only, and without intending to be limited thereto, the balance of the description may reference O_2 as the target-analyte **A** since O_2-sensitive probes are the most commonly used types of optically active probes.

First Analyte Partial Pressure Probe 21

[0035] Referring generally to Figures 2, 3 and 4A, the first probe **21** is an oxygen partial pressure sensitive probe **21** useful for optically ascertaining the partial pressure of oxygen (P_{O2}) within an enclosed space, such as the retention chamber of a hermetically sealed package **100**. The first probe **21** includes a thin film of a solid state photoluminescent composition **30** coated onto a support layer **40**. The solid state photoluminescent

composition **30** includes an oxygen partial pressure sensitive (P_{O2} sensitive) photoluminescent dye **31** embedded within an oxygen permeable polymer matrix **32**.

[0036] The oxygen-sensitive photoluminescent dye **31** used in the solid state photoluminescent composition **30** of the first probe **21** may be selected from any of the well-known P_{O2} sensitive photoluminescent dyes **31**. One of routine skill in the art is capable of selecting a suitable dye **31** based upon the intended use of the probe set **20**. A nonexhaustive list of suitable oxygen sensitive photoluminescent dyes **21** includes specifically, but not exclusively, ruthenium(II)-bipyridyl and ruthenium(II)-diphenylphenanothroline complexes, porphyrin-ketones such as platinum(II)-octaethylporphine-ketone, platinum(II)-porphyrin such as platinum(II)-tetrakis(pentafluorophenyl)porphine, palladium(II)-porphyrin such as palladium(II)-tetrakis(pentafluorophenyl)porphine, phosphorescent metallocomplexes of tetrabenzoporphyrins, chlorins, azaporphyrins, and long-decay luminescent complexes of iridium(III) or osmium(II).

[0037] Typically, the oxygen-sensitive photoluminescent dye **31** is compounded with a suitable oxygen-permeable hydrophobic carrier matrix **32**. Again, one of routine skill in the art is capable of selecting a suitable oxygen-permeable hydrophobic carrier matrix **32** based upon the intended use of the probe set **20** and the selected dye **31**. A nonexhaustive list of suitable polymers for use as an oxygen-permeable hydrophobic carrier matrix **32** includes specifically, but not exclusively, polystyrene, polycarbonate, polysulfone, polyvinyl chloride and some co-polymers. The photoluminescent composition **30** may be provided as a dispersed material, for example as aqueous suspension or powder of polymeric microparticles or nanoparticles impregnated with an oxygen-sensitive photoluminescent dye **31**.

[0038] The support layer **40** may be selected from any of the materials commonly employed as a support layer for a P_{O2} sensitive photoluminescent solid state composition **30**. One of routine skill in the art is capable of selecting the material based upon the specific analyte to be detected and the intended use of the probe set **20**. A nonexhaustive list of substrates includes specifically, but not exclusively, cardboard, paperboard, polyester Mylar® film, non-woven spinlaid fibrous polyolefin fabrics, such as a spunbond polypropylene fabric.

[0039] The support layer **40** is preferably between about 30 μm and 500 μm thick.

Second Total Pressure Probe 22

[0040] Referring generally to Figures 2, 3 and 4B, the second probe **22** is configured and arranged for optically ascertaining the total pressure within an enclosed space, such as the retention chamber of a hermetically sealed package **100**. The second probe **22** is comprised of a hermetically sealed, flexible, gas impermeable pocket or sachet **57** with a thin film of a solid state photoluminescent composition **30** sensitive to the partial pressure of a target-analyte **A** (*e.g.*, P_{O2}) and a gaseous headspace containing a known concentration of the target-analyte **A** (*e.g.*, V_{O2}^0 or P_{O2}^0) retained within the cavity **59** defined by the pocket **57**.

[0041] The cavity **59** is hermetically sealed and the pocket or sachet **57** constructed from a gas impermeable material for purposes of ensuring that the composition of the gas within cavity **59** does not appreciably change during the intended lifespan of the probe set **20**. A change in the composition of the gas within the cavity **59** can introduce significant error as both the sensor readings and the subsequent calculations utilizing those sensor readings are based upon the assumption that any change in target-analyte partial pressure results exclusively from a change in pressure, not a change in the concentration of target-analyte **A**. The pocket or sachet **57** is also sufficiently flexible to ensure that the pressure within the cavity **59** dynamically equilibrates to the surrounding pressure, thereby allowing the pressure of the gas within the cavity **59** ascertained by interrogating the second probe **22** to be equated to the pressure surrounding the probe **22**. Those of routine skill in the art are capable of selecting suitable materials for use in constructing the pocket or sachet **57**. A nonexhaustive list of suitable materials from which the pocket or sachet **57** may be constructed includes specifically, but not exclusively, polymeric films made of polyester (*e.g.*, Mylar®), polyvinylidene chloride (PVDC), polyethylene vinyl alcohol (EVOH) and laminates based on these polymers, and other films which possess or have been coated to provide very low gas permeability characteristics.

[0042] The gaseous headspace within the pocket or sachet **57** contains a known concentration of a target-analyte **A**. The amount of target-analyte **A** within the headspace need not be strictly controlled, but must be known, needs to remain substantially constant throughout the lifespan of the probe set **20**, and should fall within a concentration that provides good sensitivity over the anticipated changes in target-analyte partial pressure. For example, when the target-analyte **A** is oxygen (O_2) it is convenient to simply fill the cavity **59**

with air which contains 20.9% O_2 by volume. However, the sensitivity of the second probe **22** within higher pressure ranges can be enhanced by limiting the O_2 concentration within the headspace of the cavity **59** to a concentration of between 0.1 to 20% by volume O_2, preferably 2 to 10% by volume O_2, and most preferably between 3 to 6% by volume O_2. Concentrations below 0.1% tend to lose sensitivity due to an overly diminished quenching of the photoluminescent dye **31** while concentrations above 20.9% tend to lose sensitivity as changes in quenching of the photoluminescent dye **31** resulting from changes in P_{O2} are overwhelmed by the total quenching effect of the O_2 to which the photoluminescent dye **31** is exposed.

[0043] The solid state photoluminescent composition **30** may either be coated onto a support or lidding layer **40** as depicted in Figures 2 and 4B, or coated directly onto the interior surface of pockets **57** formed in a formable web **50**.

[0044] As with the first probe **21**, the solid state photoluminescent composition **30** includes an oxygen partial pressure sensitive (P_{O2} sensitive) photoluminescent dye **31** embedded within an oxygen-permeable polymer matrix **32**. It is generally preferred to use the same solid state photoluminescent composition **30** in both the first **21** and second **22** probes, thereby permitting the first **21** and second **22** probes to be interrogated by the same optical detection mechanism such that a single optical detector **200** can be employed to read both probes **21** and **22**.

[0045] The support layer **40** may be selected from any of the materials commonly employed as a support layer for a P_{O2} sensitive photoluminescent solid state composition **30**. One of routine skill in the art is capable of selecting the material based upon the intended use of the probe set **20**. A nonexhaustive list of substrates includes specifically, but not exclusively, cardboard, paperboard, polyester Mylar® film, non-woven spinlaid fibrous polyolefin fabrics, such as a spunbond polypropylene fabric. When the support layer **40** is also employed to hermetically seal the pocket or sachet **57** and prevent changes in oxygen concentration within the cavity **59** (*i.e.*, when the support layer **40** also functions as a blister pack lidding layer **40**), the material used as the support layer **40** needs to be gas impermeable in addition to possessing those properties and characteristics necessary to function as a support layer **40**. One such example is Mylar® film.

[0046] The support layer **40** is preferably between about 30 μm and 500 μm thick.

[0047] It is noted that the concentration of oxygen in the surrounding environment (*e.g.*, the headspace **108** of a hermetically sealed container **100**) does not impact readings taken from the second probe **22** as the photoluminescent solid state composition **30** on the second probe **22** is never exposed to the gaseous content of the surrounding environment. Hence, the second probe **22** is capable of providing accurate measurements of total pressure regardless of the complete absence or change in concentration of oxygen in the surrounding environment (*e.g.*, within the headspace **108** of a hermetically sealed container **100**).

Probe Set 20

[0048] Referring to Figures 2 and 3, the probe set **20** preferably includes an adhesive layer (preferably a pressure sensitive adhesive) **50** for facilitating attachment of the probe set **20** to a surface of a container **100** that defines an enclosed space **109** whose analyte volume fraction (V_A) (*e.g.*, V_{O2}) is to be measured, with the photoluminescent solid state composition **30** on each probe **21** and **22** facing outward from the container **100** through an area of the container **100** that is transparent or translucent to radiation at the excitation and emission wavelengths of the dye **31** in the photoluminescent solid state compositions **30** forming the first **21** and second **22** probes. The adhesive **60** may, but should not cover the photoluminescent solid state compositions **30**.

[0049] The materials of construction can be selected to provide the probe set **20** with an appropriate balancing of cost and useful lifespan. Generally, the probe set **20** should be constructed to ensure a useful lifespan of at least two to three months, preferably six to twelve months, for purposes of allowing the probe set **20** to be retained in inventory for several months prior to use and providing a probe set 20 that can remain effective from a few weeks to a few months after it has been deployed in a hermetically sealed package or container **100**.

[0050] Referring to Figure 1, the useful lifespan of probe sets **20**, more precisely the lifespan of the second probes **22**, can be increased by hermetically sealing the probe sets **20** within a gas impermeable outer package **80** along with a gaseous headspace (unnumbered) having a volume fraction of oxygen (V_{O2}) substantially the same as that within the cavity **59**

of the second probes **22** (*i.e.*, within 10%, preferably within 2% and most preferably within 0.5%).

[0051] Referring to Figures 1, 2 and 3, probe sets **20** can be conveniently produced by employing blister pack packaging technology to package a mass of a photoluminescent solid state composition **30** within hermetically sealed, flexible, gas impermeable pockets **57** to form an array of probes **10** all functional as a second probe **22**. Selected pockets **57** can then be perforated so as to place in the photoluminescent solid state composition **30** within the pocket **57** into fluid communication with the surrounding environment, thereby converting such pockets **57** from a second probe **22** to a first probe **21**. The photoluminescent solid state composition **30** can be coated onto either the lidding **40** or the formable web **50** forming each pocket **57**.

[0052] Probe sets **20** can be provided in an easily accessible and dispersible format by providing an array **10** of pockets **57** having two columns, with the pockets **57** in one column $\mathbf{10}_{\mathbf{Column\ 1}}$ formed into first probes **21** by perforating the pockets **57**, and the pockets **57** in the other column $\mathbf{10}_{\mathbf{Column\ 2}}$ formed into second probes **22** whereby each row $\mathbf{10}_{\mathbf{Row}}$ forms a probe set **20**. A line of weakness **19**, such as a line of perforations, can be provided between each row $\mathbf{10}_{\mathbf{Row}}$ so that individual probe sets **20** can be quickly and easily separated from the blister pack by machine or hand. Referring to Figure 1, the blister pack is preferably sufficiently supple to be rolled onto a core (unnumbered) for facilitating packaging, storage, shipping and handling.

Article of Commerce Equipped with a Probe Set 20

[0053] Referring generally to Figures 5, 6 and 7, a second aspect of the invention is an article of commerce comprising a product **P**, typically a labile product **P**, packaged within a hermetically sealed container **100** with a probe set **20** positioned within the headspace **108** of the container **100**.

[0054] The probe set **20** should be positioned within the headspace **108** of the container **100** so that the probe set **20** can be easily located and the P_{O2} sensitive photoluminescent solid state composition **30** of both probes **21** and **22** presented for interrogation by an analytical reader (*i.e.* a light detector) **200** through the packaging **100** and

through the various layers of material used to form the probe set **20**. Hence, at least that portion of the packaging **100** overlaying the probe set **20** needs to be transparent or translucent to radiation at the excitation and emission wavelengths of the dye **31** in the photoluminescent solid state composition **30** of both probes **21** and **22** in the probe set **20** so that the probes **21** and **22** may be interrogated by an analytical reader **200** in a noninvasive and nondestructive manner.

[0055] The ability to quickly and inexpensively monitor an analyte partial volume (V_A), such as V_{O2}, within a sealed container **100** in a nondestructive and noninvasive manner is particularly valuable when the product **P** within the container **100** is a labile product **P** that is subject to (i) target-analyte generative deterioration or spoilage, as is true for a wide variety of foodstuffs such as processed cereals, snack foods, prepared meals and meats, (ii) target-analyte consuming deterioration or spoilage, as is true for a respiring product **P**, (iii) deterioration due to a loss of pressure, such as that observed with carbonated beverages, (iv) deterioration due to loss of a specific target-analyte **A** within the headspace **108** of the container **100**, (v) subject to deterioration or spoilage in the absence of an expected increase or decrease in the concentration of a specific analyte **A** within the container **100** after the container **100** has been hermetically sealed.

[0056] It is also valuable in situations where the product **P** has been packaged under vacuum and a premature loss of vacuum can significantly affect the shelf-life of the product **P**, such as tuna vacuum packed in a gusseted pouch.

[0057] Still further, it is valuable in situations where pressure within the packaging is expected to increase or decrease shortly after the product **P** has been packaged within the container **100**, such as is observed when foodstuffs are sealed within the packaging **100** while still hot, and thereafter cooled to room temperature or below.

Manufacture

[0058] The P_A-sensitive (typically P_{O2}-sensitive) solid state composition component **30** of the first **21** and second **22** probes can be manufactured by the traditional methods employed for manufacturing such probes **21** and **22**. Briefly, the component **30** can be conveniently manufactured by (A) preparing a coating composition (not shown) which

contains the photoluminescent P_A-sensitive dye **31** and the analyte-permeable polymer **32** in an organic solvent (not shown) such as ethylacetate, (B) applying the coating composition to a surface of a support material **40** or soaking the support material **40** in the coating composition (not shown), and (C) allowing the coating composition (not shown) to dry, whereby a solid-state thin film coating **30** is formed on the support **30**. The resultant P_A-sensitive solid state composition component **30** is preferably heat treated to remove mechanical stress from the sensor material which is associated with its preparation (solidification and substantial volume reduction).

[0059] Generally, the concentration of the polymer **32** in the organic solvent (not shown) should be in the range of 0.1 to 20% w/w, with the ratio of dye **31** to polymer **32** in the range of 1:50 to 1:5,000 w/w.

[0060] A layer of pressure sensitive adhesive **60** can optionally be coated onto a major surface of the support material **40** by conventional coating techniques, and optionally covered with a release liner **70**.

[0061] The first probe **21** requires no further processing or assembly. The second probe **22** requires placement of the P_A-sensitive solid state composition component **30** within a hermetically sealed, flexible, gas impermeable pocket or sachet **57** having a gaseous headspace **59** containing a known volume fraction of the target-analyte (V_A) and capable of equilibriating to a surrounding pressure. For example, the second probe **22** can be formed by placing the P_A-sensitive solid state composition component **30** between upper and lower layers of a flexible, gas impermeable film, such as Mylar, and forming a hermetically sealed sachet **57** from the upper and lower layers of film that encloses component **30** along with a supply of a gas, such as air, having a known concentration of the target-analyte.

[0062] As referenced previously, one of routine skill in the art would also be able to produce a supply of probe sets **20** each having a first probe **21** and a second probe **22** by incorporating P_A-sensitive solid state composition component **30** within each "pocket" in a blister pack array or each "bubble" in a sheet of bubble wrap with perforation of alternating pockets or bubbles.

Use

[0063] The probe set **20** can be used to quickly, easily, accurately and reliably measure the target-analyte **A** partial volume (V_A) within a hermetically sealed package **100**. The probe set **20** can be interrogated and used to measure V_A in essentially the same manner as a typical oxygen sensitive photoluminescent probe is interrogated and used to measure the concentration of a target- analyte **A** within an enclosed space. Briefly, the probe set **20** is used to measure V_A within the retention chamber **109** of a hermetically sealed package **100** by (A) placing the probe set **20** within the retention chamber **109** at a location that is in fluid communication with the gaseous headspace **108** in the retention chamber **109** and where radiation at the excitation and emission wavelengths of the dye **31** can be transmitted to and received from the photoluminescent solid state compositions **30** with minimal interference and without opening or otherwise breaching the integrity of the package **100**, such as a transparent or translucent cap **101** on a bottle **100** or lidding **101** on a container **100**, (B) allowing the pressure within the second probe **22** to equilibrate to the pressure within retention chamber **109** of the package **100** – typically less than several seconds, (C) ascertaining partial pressure of the target-analyte **A** (P_A) within the retention chamber **109** by (i) repeatedly exposing the first probe **21** to excitation radiation over time, (ii) measuring radiation emitted by the excited first probe **21** after at least some of the exposures, (iii) measuring passage of time during the repeated excitation exposures and emission measurements, and (iv) converting at least some of the measured emissions to a target-analyte **A** partial pressure P_A based upon a known conversion algorithm or look-up table, (D) ascertaining the total pressure within the retention chamber **109** by (i) repeatedly exposing the second probe **22** to excitation radiation over time, (ii) measuring radiation emitted by the excited second probe **22** after at least some of the exposures, (iii) measuring passage of time during the repeated excitation exposures and emission measurements, (iv) converting at least some of the measured emissions to P_A within the pocket or sachet **57** based upon a known conversion algorithm or look-up table, (v) calculating the total pressure within the pocket or sachet **57** from the determined P_A and known V_A^0within the pocket or sachet **57** by applying Dalton's Law of Partial Pressure and its corollary and at least one known pair of correlated values for total pressure (P_T) and P_A, and (vi) equating the calculated P_T within the sachet **57** to P_T within the retention chamber **109** of the packaging **100**, and (E) calculating V_A within the retention chamber **109** from the values of P_T and P_A. The conversion algorithms

employed in this process are well know to and readily developable by those with routine skill in the art.

[0064] Interrogation of the probe set **20** can be accomplished in a non-destructive fashion with an external optical detector **200**.

[0065] The probes **21** and **22** may be sensitive to temperature. In order to ensure accurate measurements, readings obtained from the probes **21** and **22** may need to be adjusted to compensate for any temperature induced variation. These relationships are well known and widely published for a wide variety of target-analyte sensitive photoluminescent solid state compositions **30**.

[0066] For particular applications, the probe set **20** may be used to signal "expiration" of a packaged labile product **P** by programming the analytical instrument **200** used to interrogate a probe set **20** within a package **100** to compare the P_A, P_T and/or V_A values obtained by interrogating a probe set **20** within the packaging **100** to a predetermined threshold value indicative of product **P** expiration, and generate a signal when the value falls beyond that threshold value, indicating that the product **P** should not be sold for human consumption.

[0067] The radiation emitted by each of the excited probes **21** and **22** can be measured in terms of intensity and/or lifetime (rate of decay, phase shift or anisotropy), with measurement of lifetime generally preferred as a more accurate and reliable measurement technique, especially when seeking to establish P_{O2} via measurement of the extent to which the dye **31** has been quenched by oxygen.

EXAMPLES

Example 1

(Manufacture of First P_{O2} Probe – Polypropylene Support Layer)

[0068] One milligram of the phosphorescent oxygen-sensitive dye PtOEPK (platinum(II) octaethylporphyrinketone) was dissolved in 4 ml of 2.5% solution of

polystyrene (M.W. 280,000) in ethylacetate to form a coating composition. This composition was applied with a micropipette in 5 μL aliquots on a 155 μm thick micro porous polypropylene membrane and allowed to dry, forming an array of solid-state P_{O2} probes. Individual probes were produced by cutting the membrane into dots having a diameter of approximately 10 mm.

[0069] The P_{O2} probes were batch-calibrated using a set of standards (0 – 100% O_2 gas balanced with N_2) and a Luxcel fibre-optic detector to obtain phosphorescence phase shift readings. These readings were performed at ambient pressure and 25°C.

Example 2

(Manufacture of First P_{O2} Probe - PET/PVDC/PP Support Layer)

[0070] One milligram of the phosphorescent oxygen-sensitive dye PtOEPK (platinum(II) octaethylporphyrinketone) was dissolved in 4 ml of 2.5% solution of polystyrene (M.W. 280,000) in ethylacetate to form a coating composition. This composition was applied with a micropipette in 5 μL aliquots onto a film laminate of PET/PVDC/PP and allowed to dry, forming an array of solid-state P_{O2} probes.

[0071] The P_{O2} probes were batch-calibrated using a set of standards (0 – 100% O_2 gas balanced with N_2) and a Luxcel fibre-optic detector to obtain phosphorescence phase shift readings. These readings were performed at ambient pressure and 25°C.

Example 3

(Manufacture of Second P_T Probe)

[0072] Sachets were formed from a film laminate of PET/PVDC/PP. Each sachet was formed by overlapping two 8 x8 cm pieces of the film and heat-sealing the layers together along three sides with a double seal employing an industrial heat-sealing machine – forming a pouch with an open end. One of the P_{O2} probes formed in Example 1 was inserted inside the pouch through the open end and positioned within the pouch so that the P_{O2} probe faced the wide side and could be interrogated from outside the pouch. A styrofoam insert was placed within the pouch through the open end to ensure that the pouch retained a volume of air when sealed. The open end of the pouch was then sealed under ambient air pressure

and excess film removed with a pair of scissors to form P_T probes, each comprising a hermetically sealed sachet encasing a P_{O2} probe and a supply of air within an approximately 3x3 cm cavity.

Example 4

(Manufacture of Second P_T Probe Filled with Reduced Oxygen)

[0073] Probes were formed in accordance with Example 3 except that the pouches were flushed with a gas containing approximately 5% oxygen just prior to sealing the open end of the pouch. Performance of one of these probes was monitored, at ambient temperature and pressure in room air, using a phosphorescent phase detector over a 24 hour period. During this period no significant changes in sensor phase signal were observed, indicating that the sachet material and fabrication technology provides an effective gas-barrier.

Example 5

(Manufacture of Second P_T Probe Filled with Air)

[0074] One milligram of the phosphorescent oxygen-sensitive dye PtOEPK (platinum(II) octaethylporphyrinketone) was dissolved in 4 ml of 2.5% solution of polystyrene (M.W. 280,000) in ethylacetate to form a coating composition. This composition was applied with a micropipette in 5 µL aliquots onto a film laminate of PET/PVDC/PP and allowed to dry, forming an array of solid-state P_{O2} probes.

[0075] The P_{O2} probes were batch-calibrated using a set of standards (0 – 100% O_2 gas balanced with N_2) and a Luxcel fibre-optic detector to obtain phosphorescence phase shift readings. These readings were performed at ambient pressure and 25°C.

[0076] Sachets were formed from the film laminate of PET/PVDC/PP upon which the P_{O2} probes were formed, each containing a single P_{O2} probe on the inside surface of the sachet. Square 8 x8 cm pieces of the film were cut out and folded so as to position the P_{O2} probe between the folded layers of film. A styrofoam insert was placed between the folded layers of film to ensure that the sachet retained a volume of air when sealed, and the folded layers heat-sealed tightly with a double seal along all three sides. Excess film was removed

with a pair of scissors to form P_T probes, each comprising a hermetically sealed sachet encasing a P_{O2} probe and a supply of air within an approximately 3x3 cm cavity.

Example 6

(Use of Air Filled P_T Probe to Measure Air Induced Pressure Changes)

[0077] One of the pressure probes manufactured in Example 3 was inserted into and attached to the inner wall of a 100 ml bottle. A Luxcel fiber-optic phosphorescence phase detector was positioned to interrogate the probe through the wall of the bottle.

[0078] The bottle was sealed with an air-tight cap having an inlet and an outlet flow channel therethrough. The inlet flow channel was connected to a cylinder of compressed air. The outlet channel was closed and the internal pressure inside the bottle increased gradually by means of a pressure regulator on the cylinder of compressed air. Phase/lifetime signals were obtained from the probe by the detector at ambient pressure and at stepwise increases in pressure of 1.0 and 2.0 Bar above ambient pressure. Results are reported in Table One below. As shown in Table One, a stepwise change in phase signal was observed at each stepwise change in pressure. Such changes were in agreement with the P_{O2} calibration of the probe.

TABLE ONE

PRESSURE INSIDE BOTTLE	PHASE SIGNAL (*DEGREES*)
Ambient	11.1
Ambient + 1.0 Bar	7.2
Ambient + 2.0 Bar	3.7

[0079] Upon the release of pressure within the bottle, the phase/lifetime signal obtained from the probe quickly returned to its original value, indicating that the probe responds quickly and reversibly to changes in external pressure with a corresponding change in phosphorescence intensity and decay characteristics.

[0080] The probe was then exposed to a reduced pressure of 0.8 Bar with a concomitant increase in sensor signal (phase shift).

Example 7

(Use of Air Filled P_T Probe to Measure Carbon Dioxide Induced Pressure Changes)

[0081] Example 6 was duplicated, except that the inlet flow channel was connected to a cylinder of compressed carbon dioxide. The probe produced practically the same changes in its phosphorescent signal as when air was used to change the pressure within the bottle. This illustrates that the probes response to changes in surrounding pressure is consistent and independent from the composition of the external gas applying pressure upon the probe.

Example 8

(Use of Reduced Oxygen P_T Probe to Measure Air Induced Pressure Changes)

[0082] Example 6 was duplicated, except that a pressure probe of Example 4 was employed. Phase/lifetime signals were obtained from the probe by the detector at ambient pressure and at stepwise increases in pressure of 0.5, 1.0, 1.5 and 2.0 Bar above ambient pressure. Results are reported in Table Two below. As shown in Table Two, a stepwise change in phase signal was observed at each stepwise change in pressure. Such changes were in agreement with the P_{O2} calibration of the probe. The probe produced a distinct and reversible response to changes in external pressure, but with a larger signal change in response to smaller changes in external pressure from ambient pressure relative to the pressure probe of Example 3.

TABLE TWO

PRESSURE INSIDE BOTTLE	PHASE SIGNAL (*DEGREES*)
Ambient	21.44
Ambient + 0.5 Bar	18.77
Ambient + 1.0 Bar	16.29
Ambient + 1.5 Bar	13.61
Ambient + 2.0 Bar	11.17

Example 9

(Use of Air Pressure P_T Probe to Measure Air Induced Pressure Changes)

[0083] Example 6 was duplicated, except that a pressure probe of Example 5 was employed. The probe produced a distinct and reversible response to changes in external pressure consistent with the responses observed in Examples 6 and 7.

Claims

1. A probe set from which the volume fraction of a gaseous target-analyte in a mass can be ascertained, comprising:
   (a) a first probe comprising an optically-active, target-analyte partial pressure sensitive material configured and arranged to experience changes in target-analyte partial pressure in the mass, whereby the first probe can report target-analyte partial pressure in the mass, and
   (b) a second probe comprising an optically-active, target-analyte partial pressure sensitive material constrained to experience changes in the total pressure of the mass without experiencing changes in the volume fraction of target-analyte in the mass, whereby the second probe can report total pressure of the mass.

2. The probe set of claim 1 wherein the first and second probes are united to form a unitary probe set.

3. The probe set of claim 2 wherein the probe set is autonomously positionable.

4. The probe set of claim 1 wherein (i) the optically active material on the first and second probes is sensitive to the partial pressure of oxygen, and (ii) the first and second probes are identifiable as a first probe or a second probe.

5. The probe set of claim 1 wherein the mass is retained within a hermetically sealed chamber of a container.

6. The probe set of claim 1 wherein the second probe is a self-contained, remotely interrogatable, pressure probe including at least (i) a hermetically sealed, flexible, gas impermeable sachet capable of equilibriating to a surrounding pressure, (ii) an optically-active, target-analyte partial pressure sensitive material within the sachet, and (iii) a gaseous headspace within the sachet containing a known volume fraction of the target-analyte.

7. The probe set of claim 6 wherein the first and second probes are remotely interrogatable.

8. The probe set of claim 6 wherein the first and second probes have the same optically-active material whereby a single optical detector having a single optical detection mechanism can interrogate both probes.

9. The probe set of claim 6 wherein (i) the optically active material on the first and second probes is sensitive to the partial pressure of oxygen, and (ii) the headspace of the sachet is filled with air.

10. The probe set of claim 8 wherein the optically active material is a photoluminescent material.

11. The probe set of claim 10 wherein the photoluminescent material is based upon a long-decay fluorescent or phosphorescent dye and is sensitive to the partial pressure of oxygen.

12. The probe set of claim 11 wherein the fluorescence or phosphorescence lifetime of the photoluminescent material changes in response to changes in the partial pressure of oxygen.

13. An article of commerce, comprising: (i) a product retained within a hermetically sealed chamber of a package, and (ii) a probe set according to claim 1 within the chamber operable for sensing and reporting total pressure and target-analyte partial pressure within the chamber.

14. The article of claim 13 wherein the first and second probes are united to form a unitary probe set.

15. The article of claim 13 wherein (i) the optically active material on the first and second probes is sensitive to the partial pressure of oxygen, and (ii) the first and second probes are visually identifiable as a first probe or a second probe.

16. The article of claim 13 wherein the second probe is a self-contained, remotely interrogatable, pressure probe including at least (i) a hermetically sealed, flexible, gas impermeable sachet capable of equilibriating to a surrounding pressure, (ii) an

optically-active, target-analyte partial pressure sensitive material within the sachet, and (iii) a gaseous headspace within the sachet containing a known volume fraction of the target-analyte (V_A^0).

17. The article of claim 16 wherein (i) the first and second probes have the same optically-active material, (ii) the first and second probes bear indicia identifying each probe as a first probe or a second probe, and (iii) a single analytical instrument can identify each probe as a first probe or a second probe from the indicia on each probe, and can optically interrogate both probes.

18. The article of claim 16 wherein (i) the optically active material on the first and second probes is sensitive to the partial pressure of oxygen, and (ii) the headspace within the sachet is filled with air.

19. The article of claim 16 wherein (i) the optically active material on the first and second probes is sensitive to the partial pressure of oxygen, and (ii) the headspace of the sachet is filled with a gas containing between 0.1 and 20% oxygen.

20. The article of claim 16 wherein (i) the optically active material on the first and second probes is sensitive to the partial pressure of oxygen, and (ii) the headspace of the sachet is filled with a gas containing between 2 and 10% oxygen.

21. The article of claim 16 wherein (i) the optically active material on the first and second probes is sensitive to the partial pressure of oxygen, and (ii) the headspace of the sachet is filled with a gas containing between 3 and 6% oxygen.

22. The article of claim 17 wherein the optically active material is a photoluminescent material sensitive to the partial pressure of oxygen.

23. The article of claim 22 wherein the photoluminescent material is based upon a long-decay fluorescent or phosphorescent dye with a fluorescence or phosphorescence lifetime that changes in response to changes in the partial pressure of oxygen.

24. The article of claim 13 wherein the product is subject to gas generative deterioration or spoilage.

25. The article of claim 15 wherein the product is subject to oxygen generative deterioration or spoilage.

26. The article of claim 15 wherein the product is a respiring product.

27. The article of claim 13 wherein the product is subject to target-analyte consuming deterioration or spoilage.

28. The article of claim 26 wherein the product is a grain-based processed food subject to oxygen consuming deterioration or spoilage.

29. The article of claim 13 wherein a loss of target-analyte within the packaging is reflective of product deterioration.

30. The article of claim 29 wherein the chamber is pressurized.

31. The article of claim 13 wherein an increase in the volume fraction of target-analyte in the chamber of the hermetically sealed package after the package is sealed is desired and expected.

32. The article of claim 13 wherein a decrease in the volume fraction of target-analyte in the chamber of the hermetically sealed package after the package is sealed is desired and expected.

33. The article of claim 13 wherein the optically active material on both the first and second probes can be optically interrogated through the package.

34. The article of claim 13 wherein the optically active material is sensitive to the partial pressure of carbon dioxide.

35. The article of claim 16 wherein the optically active material is sensitive to the partial pressure of carbon dioxide.

36. The article of claim 35 wherein the headspace of the sachet is filled with air.

37. A method of determining volume fraction of a target-analyte within a hermetically sealed package, comprising the steps of:

(a) obtaining an article of commerce according to claim 13,

(b) obtaining at least one analytical instrument capable of reading the optical activity of the first and second probes,

(c) taking a reading from the first probe with an obtained analytical instrument,

(d) correlating the value of the reading to a target-analyte partial pressure value (P_A) of the hermetically sealed chamber,

(e) taking a reading from the second probe with an obtained analytical instrument,

(f) correlating the value of the reading to a total pressure value (P_T) of the hermetically sealed chamber,

(g) calculating a volume fraction of target-analyte within the chamber of the package from the values of P_T and P_A, and

(h) reporting the calculated volume fraction of target-analyte within the chamber of the package.

38. The method of claim 37 wherein the volume fraction of target-analyte in the gaseous headspace within the package is calculated by dividing P_A by P_T.

39. The method of claim 37 wherein the first and second probes are united to form a unitary probe set.

40. The method of claim 37 wherein the first and second probes are precalibrated and read with a single analytical instrument.

41. The method of claim 37 wherein the optically active material on the first and second probes is sensitive to the partial pressure of oxygen.

42. The method of claim 37 wherein the second probe is a self-contained, remotely interrogatable, pressure probe including at least (i) a hermetically sealed, flexible, gas impermeable sachet capable of equilibriating to a surrounding pressure, (ii) an optically-active, target-analyte partial pressure sensitive material within the sachet, and (iii) a gaseous headspace within the sachet containing a known volume fraction of the target-analyte (V_A^0).

43. The method of claim 42 wherein the first and second probes have the same optically-active material whereby a single analytical instrument having a single optical detection mechanism can interrogate both probes.

44. The article of claim 42 wherein (i) the optically active material on the first and second probes is sensitive to the partial pressure of oxygen, and (ii) the headspace within the sachet is filled with air.

45. The method of claim 37 wherein all readings and correlations are based upon photoluminescence lifetime of the corresponding probe.

46. The method of claim 42 wherein the second probe has been precalibrated or batch calibrated with at least one known external total pressure value before the article of commerce is obtained.

47. The method of claim 46 wherein the at least one known external total pressure value is ambient pressure.

48. The method of claim 46 wherein the first probe has been precalibrated or batch calibrated with at least one known target-analyte partial pressure before the article of commerce is obtained.

49. The method of claim 37 further comprising the steps of comparing the calculated volume fraction of target-analyte within the chamber of the package to a predetermined threshold value and signaling when the calculated volume fraction of target-analyte within the chamber of the package exceeds the threshold value, indicating that the product should not be sold for human consumption.

50. The method of claim 37 further comprising the steps of comparing the calculated volume fraction of target-analyte within the chamber of the package to a predetermined threshold value and signaling when the calculated volume fraction of target-analyte within the chamber of the package is less than the threshold value, indicating that the product should not be sold for human consumption.

51. The method of claim 37 wherein the optically active materials are optically interrogated by the at least one analytical instrument in a contactless nondestructive manner through the package.

52. The method of claim 43 wherein the optically-active material is based upon a fluorescent or phosphorescent dye.

53. The method of claim 37 wherein the product is subject to target-analyte generative deterioration or spoilage.

54. The method of claim 37 wherein a loss of target-analyte volume fraction within the chamber of the package is reflective of product deterioration.

55. A method of manufacturing the probe set according to claim 6, which includes at least the steps of:

(a) preparing a composition of a target-analyte partial pressure sensitive photoluminescent dye in a suitable carrier matrix,

(b) applying the composition to a first support material, creating a first optically active target-analyte partial pressure sensitive sensor effective as the first partial pressure probe,

(c) applying the composition to a second support material creating a second optically active target-analyte partial pressure sensitive sensor, and

(d) hermetically sealing the second sensor and a gas having a known volume fraction of target-analyte (V_A^0) within a flexible, gas impermeable sachet to form the second total pressure probe.

56. The method of claim 55 wherein the photoluminescent dye is an oxygen sensitive transition metal complex.

57. The method of claim 56 wherein the transition metal complex is selected from the group consisting of a ruthenium bipyridyl, a ruthenium diphenylphenanotroline, a platinum porphyrin, a palladium porphyrin, a phosphorescent complex of a tetrabenzoporphyrin, a chlorin, a porphyrin-ketone, an aza-porphyrin and a long-decay luminescent complex of iridium(III) or osmium(II).

58. The method of claim 56 wherein the matrix component is selected from the group consisting of silicone, polystyrene, polycarbonate, and polysulfone.

59. The method of claim 55 wherein the gas sealed within the sachet is air and the sachet is sealed at ambient pressure.

60. The method of claim 55 wherein the composition is applied directly upon an inner surface of the sachet and exposed to the gas within the sachet to form the second probe.

61. A method of manufacturing probe sets according to claim 6, which includes at least the steps of:

(a) hermetically packaging optically-active, target-analyte partial pressure sensitive material in a gaseous headspace having a known volume fraction of target-analyte within flexible, gas impermeable pockets on a blister pack, and

(b) perforating the blister pack so as to expose selective pockets to the surrounding environment and form pairs of adjacent perforated and unperforated pockets on the blister pack, whereby the perforated pockets are first probes and the unperforated pockets are second probes.

62. The method of claim 61 further comprising the step of forming a line of weakness in the blister pack so as to permit hand separation of individual pairs of adjacent perforated and unperforated pockets.

63. The method of claim 61 wherein the blister pack includes one column of perforated pockets, one column of unperforated pockets and at least five rows.

64. The method of claim 63 wherein the blister pack is formed as a roll.

65. The method of claim 61 wherein the blister pack is hermetically sealed within a gas impermeable outer package along with a gaseous headspace having a volume fraction of oxygen substantially the same as that within the unperforated pockets.

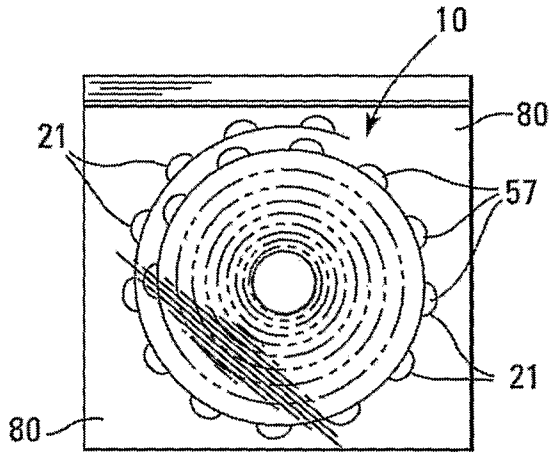


Fig. 1

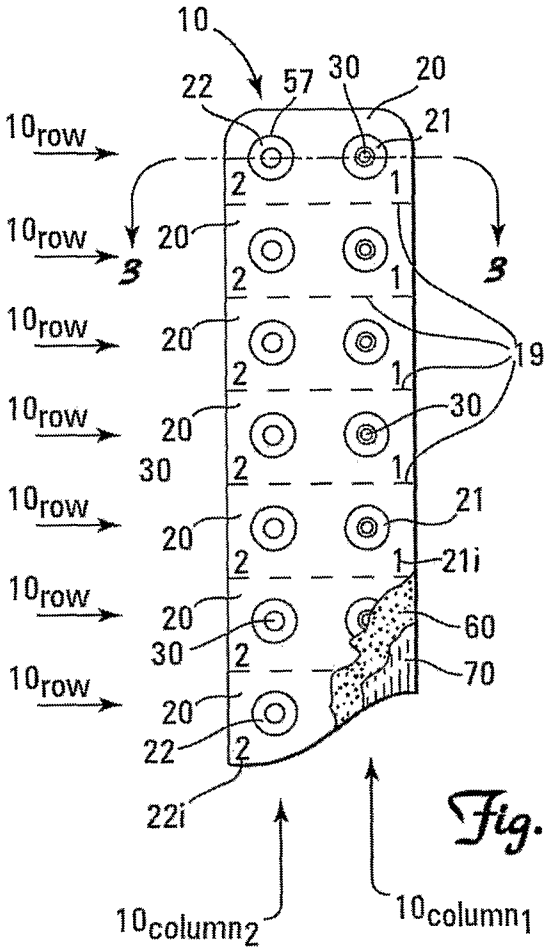


Fig. 2

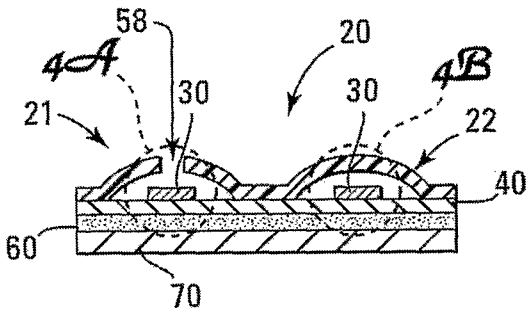


Fig. 3

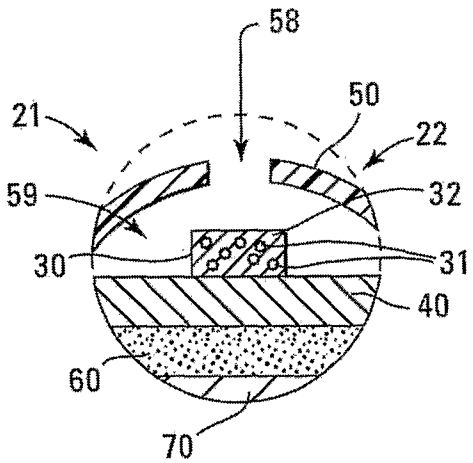


Fig. 4A

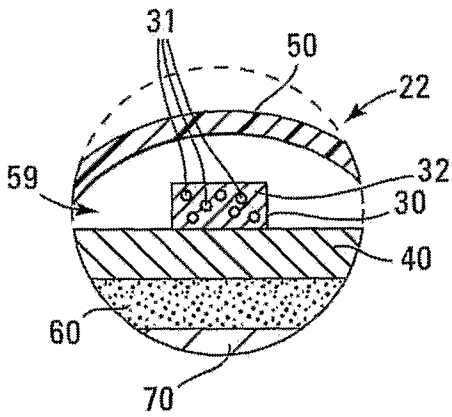


Fig. 4B

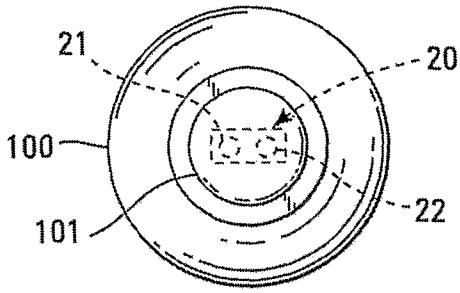


Fig. 6

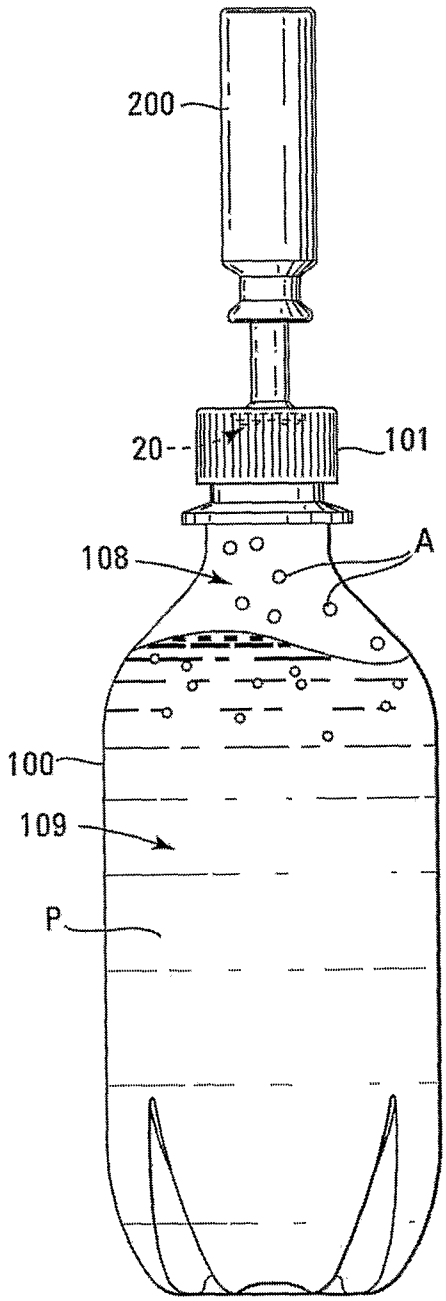


Fig. 5

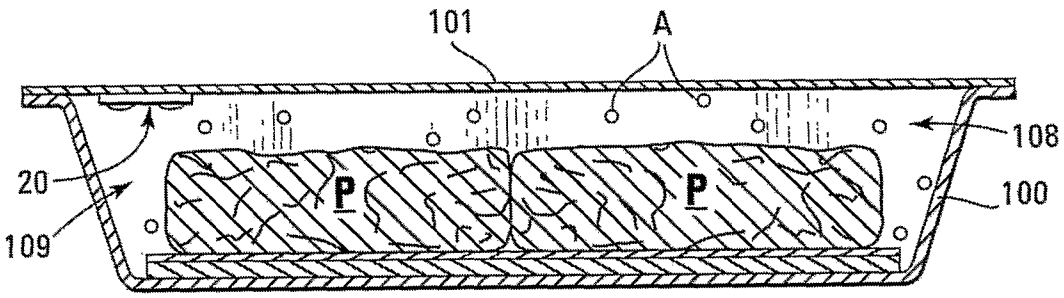


Fig. 7

INTERNATIONAL SEARCH REPORT

International application No
PCT/IE2010/000013

A. CLASSIFICATION OF SUBJECT MATTER
INV. G01N21/64 G01L11/02 G01N31/22 G01N33/00
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
G01N G01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2009/028756 A1 (SHAHRIARI MAHMOUD R [US]) 29 January 2009 (2009-01-29) cited in the application paragraph [0019] - paragraph [0022]	1-65
A	US 7 569 395 B2 (HAVENS ET AL.) 4 August 2009 (2009-08-04) cited in the application column 8, line 13 - line 38 column 14, line 4 - line 52 figures 1,11	1-65
A	US 5 407 829 A (WOLFBEIS OTTO S [AT] ET AL) 18 April 1995 (1995-04-18) column 3, line 52 - column 4, line 26 figures	1-65

-/--

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

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"P" document published prior to the international filing date but later than the priority date claimed

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Date of the actual completion of the international search	Date of mailing of the international search report
24 November 2010	03/12/2010

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Fax: (+31–70) 340–3016	Krametz, Edeltraud

INTERNATIONAL SEARCH REPORT

International application No
PCT/IE2010/000013

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2007/212789 A1 (HAVENS MARVIN R [US] ET AL HAVENS MARVIN RUSSELL [US] ET AL) 13 September 2007 (2007-09-13) paragraph [0032] - paragraph [0035] figure 1	1-65

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/IE2010/000013

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2009028756 A1	29-01-2009	NONE	
US 7569395 B2	04-08-2009	US 2007212792 A1	13-09-2007
		WO 2007106776 A1	20-09-2007
US 5407829 A	18-04-1995	NONE	
US 2007212789 A1	13-09-2007	WO 2007106778 A1	20-09-2007