Abstract: Apparatus for the measurement of the gas concentration in a sealed container comprises a laser source (10) designed to transmit a laser beam (F) at a predetermined wavelength, the source being positioned such that the laser beam passes through the optically transparent portion of the container (200) containing the mixture of gases; a detector (30) designed to detect the absorption of the laser beam (F) and output a datum representing the absorption spectrum of the gas the concentration of which is to be measured; and a second laser source (110) designed to transmit a second laser beam (F') at a predetermined wavelength, the second source being positioned such that the second laser beam passes through the optically transparent portion of the container (200) containing the mixture of gases; a second detector (130) designed to detect the second laser beam (F') and output a datum representing the absorption spectrum of the gas the concentration of which is to be measured; and a computer (140) designed to use parameters of the first and second absorption spectra to calculate the concentration of the gas to be measured.
Published:
— without international search report and to be republished upon receipt of that report (Rule 48.2(g))

Declarations under Rule 4.17:
— of inventorship (Rule 4.17(iv))
SPECIFICATION

Technical field

The present invention relates to apparatus for measuring the concentration, and preferably also the pressure, of a gas contained within a closed container, for instance a bottle, according to the features of claim 1.

Background art

Oxidation is a widespread problem in the production of beverages such as wines and beers and the chemical phenomena involved are not fully known. Knowledge of the oxygen concentration in the container may help winemakers to predict and study the ageing of wine.

The concentration of gas, for instance oxygen, in closed containers such as bottles of the type used for gaseous beverages, beer, juice and wine, is generally measured by contact, for instance by drilling through the cap and inserting a measuring device such as an oxygen sensor into the bottle. This type of measurement, although reliable and accurate, has some drawbacks as in practice the bottle's seal may be destroyed with the result that it cannot then be sold; the procedure is also slow and invasive.

In many fields of the foodstuffs industry and in particular in the wine and beverages sector there is therefore a need for apparatus for measuring oxygen which is contact-free. Contact-free measurement may be carried out without detriment to the content of the bottle and therefore repeated at will on the same container; it may also be carried out sufficiently rapidly to enable its use in an automated production line so that output as a whole can be monitored.

the automatic measurement of pressure and concentration within sealed
containers, the device comprising a laser source which transmits a laser
beam of a predetermined wavelength to an optically transparent container
and detectors which detect the laser beam which is attenuated by
absorption of the gas. The detectors supply a first datum representative of a
first absorption spectrum of the gas which includes distorted absorption
lines and noise. The invention applies a calculation method designed to
receive and process this first datum. Parameters representing a second
absorption spectrum which is free from noise and distortion in the
absorption lines are output from this operation. The pressure and the
concentration of the gas in the container may be obtained from these
parameters.

The Applicant has observed that this type of method cannot be used for gas
pressures which are too high.

"VCSEL-based oxygen spectroscopy for structural analysis of pharmaceutical
discloses a single-beam instrument based on tunable diode laser absorption
spectroscopy (TDLAS) and its use for structural analysis of pharmaceutical
solids which are highly dispersive. Using a vertical cavity laser (VCSEL) to
measure the molecular oxygen dispersed in tablets, structural properties
such as porosity are measured.

The Applicant has observed that this approach may be used only when the
gas pressure is substantially equal to atmospheric pressure.

The apparatus of the invention is designed to measure the pressure and
concentration of a gas within sealed containers such as wine and beverage
bottles without opening the container. A main object of this apparatus is to measure concentrations of gas within a range of between 0.1% and 100%, and preferably between 0.1% and 5%. This type of apparatus may be used for instance by winemakers to diagnose bottling and corking processes and the long-term conservation of the bottled wine.

These and other objects are achieved by the invention with the measurement apparatus whose main features are set out in the appended claims.

**Brief description of the drawings**

Other advantages and features of the invention will become clear from the following detailed description, provided purely by way of non-limiting example and given with reference to the appended drawings, in which:

- Fig. 1 is a block diagram relating to a detail of an operating stage of the apparatus of the invention, in particular the processing of the WMS signal;
- Fig. 2 is a block diagram relating to a further detail of an operating stage of the apparatus of the invention, in particular the digital synchronization of the modulation of the laser signal and the demodulation of the signal downstream of the photo-detector;
- Fig. 3 is a simplified diagram of a detail of the apparatus of the invention, in particular a detail to minimise retroreflection (a) or collimated light (b);
- Fig. 4 is a perspective view of a different detail of the apparatus embodied in accordance with the invention;
- Fig. 5 is a diagram illustrating the apparatus of the invention;
- Figs. 6a and 6b are perspective views, respectively overall and of a
detail on an enlarged scale, of the apparatus of the invention;
- Fig. 7 is a view on an enlarged scale of a member of the apparatus of
the invention;
- Fig. 8 shows a further preferred example of the same detail of Fig. 7;
- Fig. 9 is a graph showing a calibration curve used in the apparatus of
the invention;
- Figs. 10a and 10b show the signal processed by the apparatus of the
invention in two different operating states;
- Fig. 11 is a graph of the curve of the absorption signal of the $O_2$ line
recorded as a function of the % concentration of $O_2$;
- Fig. 12 shows a plurality of curves relating to the peak-to-peak signal
relating in each case to the same $O_2$ absorption line at constant
concentration as a function of pressure;
- Fig. 13 shows various absorption curves of the $O_2$ line recorded for
different pressures between 1000 and 2300 mbar at constant
concentration;
- Fig. 14 shows the curve of the $CO_2$ (direct) absorption lines at
constant concentration as a function of pressure from 1000 to 3000
mbar.

Preferred embodiments

Apparatus for measuring the concentration of a gas within a sealed
container is shown overall by 100 in Fig. 6.

In the appended drawings, this container is a bottle 200, although any other
type of container may be used, for instance cans and the like, in which at
least a portion of the material forming the outer casing of the container is at least partially optically transparent.

In the case of a bottle, it generally contains a liquid and there is generally a mixture of gases between the upper surface of the liquid and the stopper. In the case of wine bottles it is desirable to calculate the quantity, i.e. the concentration, of oxygen above the wine.

The apparatus 100 uses a measurement method based on tunable diode laser absorption spectroscopy (TDLAS). The apparatus 100 therefore includes a laser 10, preferably a tunable diode laser, which transmits a laser beam at a transmission frequency corresponding to the absorption frequency of an atom or a molecule of the target gas (i.e. the gas whose concentration within the container 200 it is wished to measure; the transmission frequency of the laser beam is therefore tuned so that it substantially coincides with the absorption frequency of the gas in question), the transmission frequency being in the region around 760 nm, for instance, in the case of $O_2$. This target gas is part of a mixture of gases within the container.

In TDLAS technology, as the laser 10 is such that it is possible to modify the wavelength of the beam transmitted, the laser beam which passes through the container 200 has a wavelength which varies within a predetermined interval (in the case of oxygen, for instance, this interval is equal to 0.2 nm around 763 nm); absorption by the target gas in the container is thus measured for each separate wavelength.

The apparatus 100 also includes a seat 90 to house the container 200 containing the mixture of gases, including the target gas, whose absorption
is to be measured.
In this preferred embodiment, therefore, the laser 10 may for instance be a vertical cavity surface-emitting laser (VCSEL) or a laser of the distributed feedback (DFB) type. These are lasers with single-mode transmission with a width lower than 1 GHz which are tunable by varying the temperature or the temperature junction current or the junction current.
In addition to the laser 10, the apparatus 100 includes a detector 30, preferably a photo-detector, which receives the laser beam transmitted by the laser 10 after it has passed through the container 200 and therefore also the mixture of gases contained therein. In order to collect the majority of the light output by the sample, the detector 30 of the preferred embodiment of Fig. 4, is a silicon photodiode with a large sensitive surface, although other detectors could be used as would be known to a person skilled in the art. The laser 10 and the detector 30 form the first measurement channel of the device of the invention.
The laser 10 and the detector 30 are mounted on a frame 20, and are both supported for instance at the opposing ends of a beam 55, in which the positioning of the laser 10 and the detector 30 may be adjusted, for instance by adjustment knobs or other means known per se, so as axially to move the laser/detector and to adjust the distance between them, or to carry out a vertical positioning movement. Depending on the container 200, the positioning of the first measurement channel formed by the laser 10 and the detector 30 may differ in order to coincide with the zone in which the gas mixture is present.
A support 95 is also preferably provided on which the container 200 is
positioned in order to adjust its height (i.e. the support 95 may be axially moved so as to vary the position of the container 200 along the axis Z; see Fig. 6). Preferably, it is also possible to rotate this support 95 about its axis so as to enable several possible degrees of latitude in the positioning of the container 200, the support 95 for instance comprising a chuck. The support 95 and the frame 20 are also preferably independent, i.e. there is no mechanical connection between the two members so that they are not mechanically coupled.

As shown in Fig. 3b, the apparatus 100 also includes an electronic control unit which performs a plurality of functions for the correct operation of the apparatus 100. These functions, some known in the relevant technical field and others specific to the invention, will be described in further detail below. By way of example, the electronic unit 40 carries out scanning, modulation of the signal transmitted by the laser 10, gain control, normalization and demodulation of the optical signal reaching the detector 30, all functions which are preferably fully controlled by software. The electronic unit 40 therefore includes all the calculation means for the processing operations described below.

As is known in the art, when a monochromatic light beam of intensity $I(\lambda, \zeta)$ enters an absorbent medium, the radiation transmitted through a thickness $Z$ has an intensity equal to

$$I(\lambda, \zeta) = I(\lambda) \exp(\int k(\lambda, T) \, dZ)$$

(1)

where $k(\lambda, T)$ is a positive constant known as the absorption coefficient. According to Beer's law, the absorption coefficient is proportional to the
concentration of the absorbent material. In particular:
\[ k(\lambda, T) = S_i(T) \phi(\lambda, T, P) \cdot n(p, T) \]

where \( S_i(T) \) is the total absorption per molecule for the \( i^{th} \) transition, \( \phi(\lambda, T, P) \) is the spectral line shape function and \( n(p, T) \) is the density of the absorbent molecules. \( T \) and \( P \) are the temperature and pressure respectively and \( p \) is the partial pressure of the target gas.

The density of the gas molecules, which is linked to concentration, is the value which it is wished to obtain, as the total absorption per molecule (for instance from tables) and the optical path \( z \) are known.

The spectral line is not a line of dimension equal to zero, but is a distribution of the "line of the spectrum". This distribution is commonly represented as a Lorentzian distribution, i.e.:
\[ \psi(\lambda, T, P) = \frac{(\Gamma/2)}{\pi(\lambda^2 + (\Gamma/2)^2)} \]

where \( \Gamma \) is the full width at half maximum, or FWHM, in Hertz.

In a system where broadening of the absorption line is due principally only to collisions (approximation valid at ambient temperature at pressures above 5 bar), the width in Hertz (HWHM) may be written as follows:
\[ \Gamma = \frac{4Np^2P}{\sqrt{RT} \mu \pi} \]

where \( p^2 \) is the collision section, \( N \) is Avogadro's number, \( P \) is the total pressure of the gas, \( R \) is the universal gas constant, \( \mu \) is the particle mass and \( T \) is temperature.
Equation (4) is valid in the approximation of line broadening due only to collisions valid in the operating system of the apparatus 100. Broadening is expressed here in frequency.

The apparatus 100 also operates in wavelength modulation spectroscopy (WMS) mode in order to monitor the weak absorption lines in the spectral region mentioned above and, in a possible application of this apparatus, the absorption signal of the gas, for instance oxygen, is very weak.

WMS is used to counter the conventional problems of absorption spectroscopy due to the need to measure a small variation superimposed on a signal of high intensity such as the signal from the absorption of the target gas which is particularly weak in comparison with the background noise. This WMS technique may be applied in such a way as to be extremely immune to the power and efficiency fluctuations which are always present in the tuneability interval provided by diode lasers.

Fig. 2 is a block diagram illustrating the circuitry 50 which enables the application of the WMS, which circuitry 50 is part of the electronic unit 40. The wavelength modulation measurement takes place by modulating the drive current of the laser by means of a sinusoidal signal of frequency $\Omega$ (for instance some tens of kHz) via a modulation buffer 70 with an amplitude such as to cause a maximum displacement in the transmission wavelength of the laser comparable to the width of the absorption line in question. A further modulation with a triangular wave of variable amplitude and frequency in the order of some tens of Hz is superimposed on this modulation in order to obtain several "sweeps" of the same spectral region.

For this purpose, again with reference to Fig. 2:
- a conversion card 60 operating in digital-to-analogue mode D/A converts the modulation signal;
- the signal generated by the D/A conversion card 60 is sent to the laser 10 to obtain the above-mentioned modulation with a triangular wave superimposed on a radio-frequency sinusoid;
- the signal received from the photo-detector 20 is digitized by a further card 60’ operating in analogue-to-digital mode A/D in a synchronous manner with the preceding card by means of a clock 80; the cards 60 and 60’ may coincide;
- the digitized signal is sent, normalized in amplitude and then processed with filters in the manner described below.

However, the dual modulation of the signal sent to the laser 10 means that the non-linearity of the measurement channel due to the absorption causes a distortion of the modulating signal which increases its harmonic content.

On the receiving side, the signal of the photo-detector 30 is filtered around one of the harmonics of the modulation frequency and then detected (Fig. 1).

However, converting the signal reaching the photo-detector 30 from analogue to digital provides an advantage that lies in the possibility of obtaining particularly fine comb filters through coherent sampling in the A/D and D/A sections of the instrument (Fig. 2). The signal acquired from the photo-detector 30 and supplied to the conversion card A/D is in practice subject to the following steps, performed by software:

- a coherent mean (step A of Fig. 1) is determined between multiple scans (a scan is the input signal in Fig. 1), allowing a substantial
improvement of the signal-to-noise ratio;
- narrow band (super-Gaussian) filtering is carried out (see block B of Fig. 1) about the second harmonic of the modulation signal so as to obtain the signal to be demodulated without introducing phase distortions and without degrading the shape of the trace;
- a demodulation of the signal thus obtained is carried out by baseband translation (block C in Fig. 3), with the application of a phase rotation sufficient to compensate for the modulation delays introduced by the laser and current driver assembly;
- a fitting of the signal thus obtained is carried out (block D), for instance by means of least-squares or matched filter fitting with reference absorption profiles, depending on the range of operating pressures required of the instrument; the fitting carried out is typical of the invention and will be described in detail below;
- the measurement of the concentration of the gas is then carried out by analysing the signal obtained after steps A-D as described below.

This type of signal processing, i.e. the method of modulation and demodulation of the signal, is also known from T. Svensson, M. Andersson, L. Rippe, S. Svanberg, S. Andersson-Engels, J. Johansson, S. Folestad, "VCSEL-based oxygen spectroscopy for structural analysis of pharmaceutical solids", Appl. Phys. B 90, 345-453 (2008), which is incorporated here. This article nevertheless uses filters differing from those of the present invention.

In addition, the synchronous mean operation between a plurality of scans of step A of the above description carries out a comb filtration of the signal
detected by the detector 30, attenuating any component of disturbance which is not synchronized with the scanning signal. The type of signal obtained after each step of Fig. 1 is shown diagrammatically in Fig. 1 below each corresponding block.

The main problem raised by TDLAS-WMS methods lies in the interpretation of the data acquired, i.e. in the interpretation of the demodulated signal, for instance the signal demodulated in the manner described in steps A-C of Fig. 3, which interpretation generally requires sophisticated algorithms for the simultaneous detection of total pressure and concentration of the species in question from the shape and intensity of the absorption signal. Once the absorption spectrum of the gas whose concentration it is desired to know has been obtained by means of the first channel, it is therefore extremely complex simultaneously to obtain both the pressure value and the concentration value from this spectrum. As is known in the art, in WMS-TDLAS the demodulated wave shapes (assuming a small depth of modulation) are an approximation of the $n^{th}$ derivatives of the absorption profile, where $n$ is the magnitude of the demodulated harmonic; from measurements of the width of the peaks present in the demodulated wave shapes it is possible, by calibration, to trace the pressure of the sample being examined; the concentration is nevertheless obtained from the amplitude of the demodulated signal as the pressure is known.

For instance, Fig. 11 shows the curve of the absorption signal of the $0_2$ line recorded as a function of the % concentration of $0_2$ in the neck space of a bottle at a constant pressure of 1016 mbar. It can be seen that there is optimum linearity and low data dispersion.
While it is possible in direct absorption spectroscopy to use a simple fitting algorithm to relate the signal acquired to a theoretical model of the absorption lines, in the case of WMS the situation is complicated because of the interaction between the width of the line and the depth of wavelength modulation applied to the laser. With reference to Fig. 13, the drawing shows various absorption curves of the \( O_2 \) line recorded for various pressures from 1000 to 2300 mbar at constant concentration. The shape of the line is characteristic of the derivative spectroscopy measurement (second derivative), as mentioned above. It will be noted that the shape of the line depends to a certain extent on pressure. Obtaining the concentration and pressure values, in particular for high pressures, from a single measurement is not therefore reliable.

According to the invention, to resolve this problem, two measurement channels are used to obtain the total pressure and concentration values of the gas in question. The first channel is formed by the diode 10 and the detector 30, and the second is described below. The peak intensity of the absorption signal of the gas in question may be obtained from an analysis of the above-described demodulated wave shapes obtained in the first channel by peak measurement in respect of the signal or in respect of a version obtained by fitting or matched filter to increase sensitivity in the case of low S/N ratios. The concentration value is then obtained from the peak intensity by applying a calibration curve, subsequently phase analysed, as the pressure is known (information obtained via a second channel and a second absorption spectrum, as will be described in further detail below). The calibration curve in practice shows the peak intensity value with which the
instrument responds for a known concentration, as pressure varies. Therefore, given the pressure (calculated in the manner described below) and having calculated the peak intensity of the spectrum of the gas whose concentration it is wished to measure (by measurement of the signal or its processing as described below), the desired concentration value is obtained from the above-mentioned calibration curve.

Fig. 9 shows a calibration curve for a plurality of pressures and peak-to-peak amplitudes of the signal, for an oxygen concentration of 20%. This drawing is a single curve of Fig. 12 (Fig. 12 is at constant concentration), which shows how the signal relating to the same $O_2$ absorption line decreases as the pressure varies from 1000 to 4700 mbar. The data are taken at constant concentration. It can be seen that at high pressures it is very difficult to determine the pressure because the signal tends to move closer to the base signal shown by the horizontal line.

The curve of Fig. 9 belongs to a family of curves obtained for different concentrations of the target gas whose concentration it is wished to know (a curve = a specific gas concentration), curves which are saved in a memory of the apparatus. Once the peak value of the signal given by the first channel and the value of the total pressure of the gas mixture given by the second channel are obtained, a (single) curve is therefore identified from the two points and belongs to the above-mentioned family of calibration curves and, from this identification, it is possible to obtain the concentration value of the target gas (since a curve corresponds to a specific gas concentration).
According to a preferred feature of the invention, a matched filter (see also block D of Fig. 3) is used on the signal reaching the photo-detector 30, which is an linear time-invariant filter with the characteristic of maximizing the signal-to-noise ratio output in the case of an input formed by a pulse of known shape. The pulse response which verifies this condition is given by the combined time-inverted assembly of the model pulse; in this case, the model is represented by the second derivative of the Lorentzian function from equation (3); this function is the shape of the spectral line (and it is known that this second derivative is a good approximation of the signal as detected and filtered by the apparatus 100). Simplifying equation (3):

$$\phi(\lambda, T, P) \propto \frac{1}{\lambda^2 + 1}$$

for which the second derivative is given by

$$\phi'(\lambda, T, P) \propto 2 \cdot \frac{3\lambda^4 + 2\lambda^2}{(\lambda^2 + 1)^4}$$

This curve is also called "second harmonic".

It is also possible to implement a more accurate model which takes account of the non-ideal situation due to the finite depth of modulation. This model does not consist in the $n^{th}$ analytical derivative of the Lorentzian function, but is obtained through a filtering of the absorption profile with a pulse response designed to model the effect of the interaction between the modulated source and the absorption line.

This latter type of matched filter is described in detail in R. Arndt, "Analytical lineshapes for Lorentzian signals broadened by modulation", J. Appl. Phys., 36, 2522-2524 (1965)
and


Fig. 10a shows the superimposition of the signals received from the detector 30 of the first channel and demodulated as described in respect of thirty-eight different measurements (arbitrary units proportional to the wavelength are shown on the abscissa and arbitrary units proportional to the second harmonic signal intensity, normalized with respect to the amplitude RMS of the input signal, are shown on the ordinate): Fig. 10b shows the signals of the same measurements processed with the matched filter in which a substantial reduction of noise can be seen.

As a result of the digital modulation-demodulation techniques to improve the signal-to-noise ratio as described, measurements may be also be carried out in the case of absorbances lower than \(3 \times 10^{-6}\).

By means of the preferred features of the invention, i.e. a digital management of the signal obtained from the detector 30, and the presence of the matched filter, the "noise" components in the signal detected are minimized. However, as mentioned above, in measurements by TDLAS the measurement of total pressure and concentration from the "simil-derivative" shape of the absorption profile (see equation (4)) of a gas (in this case the gas whose concentration it is wished to know) may be very difficult in the case of small concentrations (for instance below 5%, typical of the oxygen concentration in wine bottles), as a result of the brevity of the optical path.

To improve the operation of these systems, the apparatus 100 of the
invention incorporates a second measurement channel (see Fig. 6 and Fig. 5) based on direct absorption TDLAS with a second laser source 110, for instance a VCSEL laser, and a second detector 130, also preferably a photodiode.

The second channel may for instance be formed by a VCSEL operating around 2 μm for the detection of carbon dioxide with an extended InGaAs photodiode.

This second measurement channel may be configured in a direction at right angles to the first, i.e. the laser 110 and the photodiode 130 are disposed substantially at 90° with respect to the direction defined by the first laser 10 and the first photodiode 30. Any other configuration nevertheless falls within the scope of the present invention. Obviously, the laser 110 and the photodiode 130 are disposed with respect to the frame 20 and the container so that the laser beam transmitted by the laser 110 passes through the mixture of gases in the container 200 containing the gas whose concentration it is wished to know.

A channel defined in this way is used to measure the total pressure of the gaseous mixture in the container 200 which needs to be used for the calculation of the concentration of the target gas.

This measurement of total pressure, to be used in conjunction with the calibration curve and the peak intensity of the first spectrum, is obtained from the absorption profile of another gas (for instance CO₂ or H₂O) contained in the mixture of gases in the container 200. For instance, a measurement method for calculating the pressure from the absorption profile of a second gas is disclosed in International Patent Application WO
2008/053507 (i.e. the measurement method for obtaining the value of the total pressure of the gas is as described in this patent application). This method may be used for instance in the present invention, although any other method of TDLAS spectroscopy may be used.

The second channel preferably uses a direct spectroscopy method.

Fig. 14 shows the curve of the (direct) absorption lines of CO₂ at constant concentration as a function of the pressure from 1000 to 3000 mbar. The lines are in the 2 micron band. There is good sensitivity as regards pressure.

In Fig. 5, the two channels are shown diagrammatically, the first channel transmitting a laser beam F and the second channel transmitting a second laser beam F', with detectors 30, 130 for the acquisition of the two absorption spectra.

The total pressure is thus detected from the analysis of the absorption spectrum of the gaseous CO₂ present in the mixture, or, as mentioned above, of another gas (another target gas may for instance be water vapour), the measurement being obtained via the second channel (the measurement of the absorption spectrum of the second gas is preferably carried out in the manner described in Patent Application WO 2008/053507 or by direct spectroscopy).

This second part of the instrument may be a stand-alone device not connected to the first, although incorporation in the same frame is the preferred arrangement. In this operating mode, the total pressure is obtained by measuring the width of some absorption lines of the second gas contained in the mixture (e.g. CO₂) and the value is used to measure the
concentration of the target gas (e.g. \( \text{O}_2 \)) by applying the calibration curve to
the intensity value of the absorption characteristic of the target gas.

The calibration curve (example in Fig. 7), obtained from a series of
measurements conducted in the presence of fixed concentrations and
known pressures, is useful for compensating the variation of the
instrument's response as a function of pressure. This curve is obtained at
the calibration stage, with various measurements carried out as pressure
varies, by injecting the target gas (for instance oxygen) at constant
concentration into a test container provided with a conventional manometer.

A curve for each concentration is then recorded permanently in the
apparatus 100, so as to obtain a family of recorded curves.

It is important to note that the peak absorbance of the most intense lines in
the 763 nm band for \( 0.2\% \) of \( \text{O}_2 \) contained in a typical bottle neck (typical
container used in the present invention) is approximately \( 1.7 \times 10^{-6} \), which
is the detectability limit of the apparatus.

According to a particular preferred feature of the invention, in order further
to reduce the noise of the signal obtained by means of the first channel, the
apparatus 100 comprises at least one gasket 80 which is positioned as
described in detail below so as to be traversed by the laser beam which is
transmitted and propagated between the laser 10 and the container 200.

Preferably, a further gasket 80a (or, as an alternative, only this second
gasket is used) is provided and positioned so as to intercept the laser beam
after it has passed through the container 200 until it reaches the detector
30. This configuration, i.e. the inclusion of at least one gasket 80/80a,
prevents the introduction of air from outside the container and reduces
parasitic reflections and resonant cavity phenomena (etalon effect) which cause noise in the signal reaching the photo-detector 30. In particular, in a preferred configuration, air-proof optical contacts are provided between the apparatus 100 and the container 200 through two deformable gaskets 80, 80a of transparent silicone rubber (Fig. 4).

Fig. 4 shows the elastomeric gaskets 80, 80a on an enlarged scale. Fig. 7 in particular shows the gaskets for the laser 10 and photodiode 30 designed for an optical geometry of free expansion in contact with Bordeaux-type bottles (these are the same gaskets as used in Fig. 4 mounted in the apparatus 100). The squares visible in the background have a dimension of 5 mm.

The geometry of each gasket 80 is modified so as to enable full shape-coupling between the outer surface of the laser 10 and the outer surface of the container 200 on which it is supported. The purpose of the gasket is to minimize the optical disturbance caused by gases external to the mixture of gas in the container 200 along the optical path of the laser beam. The best possible contact therefore has to be provided and the surface of the laser/container and the corresponding surface of the gasket also have to be complementary.

Similarly, this correspondence is also provided in the gasket 80a interposed between the photodiode 30 and the container 200, which gasket is designed to intercept the laser beam emerging from the container over its entire optical path.

The materials used for the production of the gaskets 80, 80a are preferably optically transparent rubbers, for instance:
Prochima, Crystal Rubber (dual-component, polyaddition transparent silicone rubber, vulcanization at ambient temperature, refraction index of approximately 1.4);

Dow Corning, JCR6122 (dual-component transparent silicone rubber, highly transparent, refraction index 1.4, vulcanization at 150°C).

According to a further preferred embodiment of Fig. 8, the gasket 80 comprises a spherical collimation lens (not shown) to collimate the laser beam emerging from the laser 10, for instance a lens of sapphire glass with a diameter of 8 mm suspended in the elastomer. The squares visible in the background have a dimension of 5 mm.

Alternatively, a collimation lens is included within the packaging of the laser 10 itself, so as to transmit a collimated laser beam.

The use of these materials combined with optics in glass with a high refraction index (for instance sapphire) makes it possible to obtain collimated measurement beams and resilient instrument-sample couplings with low retroreflection.

As a result of the gaskets 80, 80a the retroreflection caused by the container are reduced as the refraction index is adapted to the apparatus-container interfaces, i.e. avoiding large index jumps. For instance, in the case where the bottle is of glass, a refraction index of approximately 1.4 is selected and is therefore close to that of the glass of the bottle, the output port of the laser and the protective covering of the sensor. Preferably, given the refraction index of the container 200 containing the gas to be examined, the refraction index of the gasket is equal to that of the container ± 0.1.

Preventing retroreflection helps to reduce the etalon effect which
substantially limits the sensitivity of the apparatus. It is known in practice that in a collimated laser beam, reflections and scattering are present in the device substantially at every interface. The various rays making up the starting beam but which have been reflected in different ways have a different phase from one another as a result of their different optical path and thus comprise interference phenomena causing a variation of intensity in the signal detected by the photodiode.

As an alternative, again to minimize retroreflection, collimation of the laser beam may be avoided: the difference between the rays of the beam in an apparatus 100 in which the laser beam F is not collimated and one in which the beam F is collimated is shown in Figs. 3a and 3b respectively. In the first case, Fig. 3a shows the optical emission of the laser and the retroreflection of the first surface of the container and of those of the photodetector. In the second case, Fig. 3b shows the collimated configuration which, if applied without the arrangements described above, would give rise to external resonant cavities and therefore disturbances of the etalon type.

Subsequently, again by means of the gaskets 80, 80a, external air is substantially excluded from the optical measurement path, which is very useful in the case of applications where there are very low concentrations of the gas whose concentration is to be measured in the container 200. For instance, the oxygen concentrations commonly present in bottles are generally in a range of 1% (or lower) to 20%, and have absorbance values comparable with the uncertainty introduced by the shape irregularities of the external surface of the container in question. It should also be borne in mind that in the case of low concentrations and high pressures in the
container 200, it would be particularly difficult to separate the two contributions of the internal-external gas as a result of the superimposition of two absorption profiles characterized by a different line width.

A possible alternative for eliminating the contribution due to the gas, for instance oxygen, external to the container is to insert the container and opto-electronics in a leak-proof chamber filled with nitrogen, rather than using the gaskets 80/80a.

In order further to reduce the residual interference effects in the optical path (which are generally of an intensity which continues to be greater than the weak absorption signal), a small vibrating motor (not shown) is secured to the frame for the laser-detector of the first channel, for instance a motor with an eccentric flywheel which has proved useful in destroying the geometrical coherence on successive means of the optical paths due to parasitic reflections. The motor is secured for instance to the upper beam 55 which supports the laser 10 and the detector 30, which beam is thus subject to vibration and causes a vibration in the first channel, while the container 200 is stable in the support 95 and is in contact with the frame 20 solely via the gaskets 80, 80a. In this way, the optical path difference is mechanically modulated and when the spectrum is averaged, the etalon effect is reduced to almost zero.

In this preferred embodiment, in which the motor which provides the vibration is included in the apparatus 200, the gaskets 80, 80a also have the function of efficient coupling of the vibration of the vibrating motor to the first channel, i.e. of the motor to the optical scheme of the cavities formed by the different optical surfaces. The gaskets may also be readily
replaced if necessary.

The variable attenuation of the optical signal caused by the container 200 does not influence the TDLAS measurement in the first channel as the intensity of the amplitude modulation imposed on the optical signal is used as a normalization reference. The apparatus 100 in practice carries out a normalization of the measurement using the mean quadratic value of the amplitude (RMS) of the signal acquired from the A/D section (digitally converted signal of the detector 30, as mentioned above, see Fig. 2). A gain control programmable by software is also provided to make use of the entire dynamic of the A/D converter (Fig. 2) irrespective of the type of container 200 to be measured. This is an automatic gain control carried out by a digital switch (not shown) which varies the transimpedance of the amplifier stage of the photodiode 30 in order to keep the amplitude of the signal acquired within predetermined limits to avoid saturation (in the case of excessive gain) or low signal-to-noise ratio (in the case of insufficient gain). The coupling of the signal received from the photodiode 30 to the successive stages of amplification and acquisition takes place in AC since the strong baseband component of the signal is of no interest for the measurement (which uses only the first and second harmonic components If and 2f) and would limit resolution during digitization. The optical signal in respect of the photodiode 30 is in practice formed by a strong DC component due to the power transmitted by the laser 10 and by a triangular fluctuation at the scanning frequency due to the wave shape which carries out the wavelength scanning by modulation of the laser current. These two components, of strong intensity with respect to the sinusoidal modulation,
are of no interest for the WMS measurement.

The apparatus as developed has also proved able to operate in situations in which there is an extremely low signal-to-noise ratio, typical of dark glass bottles; a high level of immunity has also been obtained with respect to the disturbances introduced by ambient lighting.
CLAIMS

1. Apparatus (100) for measuring the concentration of a gas in a sealed container (200) at least a portion of which is optically transparent, the container (200) containing a mixture of gases including the gas to be measured, the apparatus comprising:

- a tunable laser source (10) designed to transmit a laser beam (F) at a predetermined wavelength, the source being positioned such that the laser beam passes through the optically transparent portion of the container (200) which contains the mixture including the gas whose concentration is to be measured,

- a detector (30) designed to detect the laser beam (F) which is attenuated by the absorption of the gas whose concentration is to be measured, the detector (30) transmitting as output a datum representing an absorption spectrum of the gas whose concentration is to be measured, the laser source (10) and the detector (30) forming a first measurement channel,

characterized in that it further comprises:

- a second laser source (110) designed to transmit a second laser beam (F’) at a predetermined wavelength, the second source being positioned such that the second laser beam passes through the optically transparent portion of the container (200) containing the mixture of gases,

- a second detector (130) designed to detect the second laser beam (F’) which is attenuated by the absorption of a second gas in the mixture, this second detector (130) transmitting as output a datum
representing a second absorption spectrum of the second gas, the second laser source (110) and the second detector (130) forming a second measurement channel,
- a calculation device (40) designed to use parameters of the first and second absorption spectra to calculate the concentration of the gas to be measured,
- wherein this calculation device (40) is designed to calculate the pressure of the mixture of gases in the container (200) from the parameters of the second spectrum acquired from the second measurement channel and, using this pressure value, to obtain the concentration of the gas whose concentration is to be measured from the parameters of the spectrum of the gas whose concentration is to be measured.

2. Apparatus (100) according to claim 1, wherein the laser source (110) is a tunable laser source for carrying out a direct absorption spectroscopy measurement.

3. Apparatus (100) according to claim 1 or 2, wherein the laser source (10) is a tunable laser source for carrying out an absorption spectroscopy measurement using a tunable diode laser TDLAS and a wavelength modulation signal WMS is supplied to the laser source (10) in order to obtain a modulated laser beam.

4. Apparatus (100) according to claim 3, wherein the modulation signal to the laser source (10) is analogue and the corresponding signal from the detector (30) is converted into a digital signal.

5. Apparatus (100) according to one or more of the preceding claims,
including a gasket (80; 80a) disposed between the laser source (10) and the container (200) and/or between the container (200) and the detector (30) so as to intercept the laser beam (F) over its entire optical path between the laser source (10) and the container (200) and/or between the container (200) and the detector (30).

6. Apparatus (100) according to claim 5, wherein the gasket (80) includes a converging lens in order to converge the laser beam (F) before it enters the container (200).

7. Apparatus according to claim 5 or 6, wherein the index of refraction of the gasket (80; 80a) is equal to the index of refraction of the material from which the container (200) is made ± 0.1.

8. Apparatus (100) according to one or more of the preceding claims, wherein the calculation device (40) obtains the value of this concentration by obtaining the total pressure of the mixture from the parameters of the second absorption spectrum and calculating the intensity of the peak of the absorption spectrum line of the gas whose concentration is to be measured provided by the first channel.

9. Apparatus according to one or more of the preceding claims, wherein the calculation device (40) includes a memory in which a plurality of calibration curves is stored, each curve relating, for a specific concentration value of the gas whose concentration is to be measured, the values of the peak of the absorption line of the first absorption spectrum with the values of the total pressure of the mixture of gases contained in the container (200).

10. Apparatus (100) according to one or more of the preceding claims,
including a motor designed to cause the apparatus (100) to vibrate.