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Non-intrusive headspace gas measurements by laser spectroscopy – Performance validation by a reference sensor

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ABSTRACT

The oxygen concentration in the headspace of a large number of liquid food containers is assessed with non-intrusive diode laser absorption spectroscopy. The results are compared to those given by a traditional intrusive measurement method. The upper portions of the containers are made of translucent but non-transparent plastic materials, through which the laser light is diffusively transmitted. Measurements are performed both on packages with modified atmosphere and with normal air conditions. It is concluded that the novel non-intrusive technique provides oxygen concentrations that generally differ by less than one percentage point from the reference sensor values.

1. Introduction

Packaging is vital for keeping product quality and maintaining shelf-life of food. This is especially important for fresh and chilled products that are more sensitive to deterioration. Deterioration processes hasten by the presence of light and oxygen and also by temperature exposure (Hernandez, 2001). In order to slow down these processes, package headspaces are frequently filled with a modified atmosphere in order to reduce the oxygen content in direct contact with the packed food. The package integrity is therefore vital in order to avoid transmission of oxygen from the outside environment into the package headspace, and is thus a key parameter to monitor.

Modified atmosphere packaging is a standard procedure in the food industry in order to increase the product shelf-life, to satisfy consumers requirements for fresh food, and to facilitate the constant strive for reducing material and product waste and to reduce transports, thus considering both economic and environmental aspects. Research in this field can gain great advantage from the availability of an instrument able to measure gas concentrations in a non-intrusive manner. In this way, food and packaging quality as well as aging can be assessed during the whole shelf-life of the product, without sample waste. Optical techniques, with properties of being non-intrusive, remote and exact (Linnerud et al., 1998), fit well to the task. One common approach is to utilize the spectroscopic feature of specific light absorption by matter, accessible by, e.g., laser light, to detect and quantify different elements of an unknown sample. Each element – solid, liquid or gaseous – absorbs a unique combination of parts of the electromagnetic spectrum; the visible and infrared spectral ranges are commonly used. Solids and liquids absorb with spectrally broad and smooth features, while gases absorb in narrow, sharp, lines. These different behaviors allow access to the gas phase properties without influence by the solid and liquid phases. A well suited light source for this type of spectroscopic gas studies is a diode laser. Diode lasers are relatively cheap, efficient, easy to handle, compact and robust (Saleh and Teich, 2007). The general method employed in this study is commonly referred to as Tunable Diode Laser Absorption Spectroscopy (TDLAS) (Lackner, 2007) and the specific variety when the method is employed on light scattering samples is named GAS in Scattering Media Absorption Spectroscopy (GASMAS) (Lewander et al., 2011; Svanberg, 2010). In this study, a diode laser with a wavelength that can be tuned over a part of the spectrum where oxygen absorbs is used to evaluate the concentration of oxygen in the headspace of 345 plastic top packages for liquids.

Abbreviations: TDLAS, Tunable diode laser absorption spectroscopy; WMS, Wavelength modulation spectroscopy; GASMAS, Gas in scattering media absorption spectroscopy; PD, Photo diode; PMT, Photo multiplying tube.

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The purpose of this paper is to prove the use of laser spectroscopy for measuring headspace oxygen content in a series of liquid food packages and to compare this method with a well established, but intrusive, reference sensor based on extracting gas for external electro-chemical analysis.

The paper is organized by starting with a background to the non-intrusive technique used. We will then shortly describe the principles of the laser spectroscopic technique and give a general description of the experiments performed on the packages in this study. We then present measurements performed on five different package types together with the results, and some connecting discussion, each package type in its own section. After that we will provide some final discussion and conclusions.

2. Basic principle and experiment description

2.1. Basic principle of the technique used

The gas sensing technique is based on light absorption by gases, and the fact that each gas absorbs light in a unique way. In this study, the gas of interest is oxygen (O₂), which has a number of absorption lines at light wavelengths around 760 nm. Thus, by choosing a laser which can be tuned in wavelength in this region, these lines, and thus the gas itself, can be analyzed. The most essential parts of any TDLAS setup is a diode laser and a light detector, as presented in Fig. 1. The fraction of light that is lost at the absorbing wavelength will depend on the path length and the concentration of the gas. If the path length is known the concentration can be found and vice versa. This relationship is given by the Beer–Lambert law (Eq. (1)).

\[ I = I_0 \exp(-k \cdot c \cdot L) \]

Here, \( I \) is the light intensity at the detector, \( I_0 \) is the intensity from the laser, \( k \) is an inherent and constant property of the absorption line of the gas, \( L \) is the path length through gas and \( c \) is the concentration of the gas.

If the absorption is small, sensitivity-enhancing methods have to be applied. In this study, wavelength modulation spectroscopy (WMS) (Supplee et al., 1994) was employed. Our implementation of this method was entirely done by digital signal processing in order to achieve greater noise rejection and immunity to variations in the received power due to the sample material. The WMS method is well established in the research field (e.g., Moses and Tan, 1977) and an extensive description of the digital version used is found in (Andersson et al., 2007; Svensson et al., 2008).

2.2. Description of the experiments

A diode laser (Toptica, Model LD-0763-0050-DFB-1) with an output power of around 30 mW was used to detect oxygen in the headspace of a number of packages for liquids. A custom made computer program based on the software LabVIEW was used in connection with a DAQ-card (National Instruments, Model 6120) to control the output of the laser and synchronously sample the signal from the light detector. A schematic of the setup is shown in Fig. 2. The light from the laser was illuminated onto one of the top surfaces of the package. The plastic material of the packages will reflect or absorb most of the light, but a small fraction is diffusively transmitted through the plastic and into the package. The diffusely transmitted light will be scattered in the headspace before most is, again, absorbed by the plastic or liquid. However, a minor fraction of the total light will reach the detector (a large-area photo diode (PD), Hamamatsu, Model S3204-08, 18 × 18 mm², or Photomultiplier tube (PMT), Hamamatsu, Model R5070A, active diameter 23 mm) placed on the opposite side of the headspace (see Fig. 2). Even if most light is lost due to scattering and absorption by the solid material of the package and the liquid inside, any gas absorption in the light received by the detector is easily found due to the much more distinct and sharp features of a gas absorption imprint. To avoid the light absorption signal being affected by the atmosphere outside of the package, the short but unavoidable distance (~5 mm) between the laser and the package is flushed with nitrogen gas. Further, to suppress interference effects in the light, which could potentially make the signal noisy, the laser mount was vibrated with a small cell phone vibrator.

Since the path length of the light travelled inside the headspace is primarily unknown during a GASMAS measurement, the
obtaining the concentration is presented in the following section. However, since packages of the same model are more or less identical\(^1\) we solve the problem by initially performing calibration measurements on packages with known concentration and from this calculate the effective path length, \(L_{\text{eff}}\), of light travel inside each package model. The exact procedure for obtaining the concentration is presented in the following section.

2.2.1. Obtaining the concentration

The primarily obtained result from a GASMAS measurement is the absorption fraction, \(A = 1 - I/I_0\). To convert this into a concentration we perform a set of calibration measurements (in principle only one is needed but several can be used to get a more robust model) on packages with known concentration. The concentration could be known, either, by assuring the package contains oxygen of ambient concentration (\(\sim 21\%) or by performing subsequent measurements with a well calibrated reference sensor. In that way there is access to all variables except \(I\), in Eq. (1), and the effective path length, \(L_{\text{eff}}\), can be calculated according to Eq. (2).

\[
A_{\text{cal}} = 1 - \frac{I}{I_0} = 1 - \exp(-k \cdot c_{\text{cal}} \cdot L_{\text{eff}}) \iff L_{\text{eff}} = -\frac{\ln(1 - A_{\text{cal}})}{k \cdot c_{\text{cal}}}
\]

Here, subscript ‘cal’ indicates a value obtained from a calibration measurement. The unknown concentration can thereafter be evaluated from a measurement on an identical package with the help of the calculated effective path length, through Eq. (3).

\[
c_{\text{eval}} = \frac{\ln(1 - A) - \frac{\ln(1 - A_{\text{cal}})}{\ln(1 - A_{\text{cal}})} - k \cdot \ln(1 - A_{\text{cal}}) / (-k \cdot c_{\text{cal}})}{\ln(1 - A_{\text{cal}}) / k \cdot c_{\text{cal}}} \approx \frac{A - c_{\text{cal}}}{A_{\text{cal}}}
\]

From the result we notice that the inherent (intensive) property of the gas, \(k\), becomes irrelevant for the concentration evaluation.

2.2.2. Measurements performed

Measurements were performed on a total of 345 packages of different types (although similar in their basic structure, with HDP, High Density Polyethylene, or LDP, Low Density Polyethylene tops) with different liquid contents – some specifically made for these tests. The oxygen concentration of a subset of the packages (in total 177) was then measured with a standard, intrusive, measurement device (PBI DanSensor, Model Checkmate 9900). The concentrations evaluated with the laser technique and the reference sensor were then compared to explore the potential of the non-intrusive technique. As long as nothing else is stated, the integration time for each GASMAS measurement was 20 s for each GASMAS measurement to assure a reproducible measurement geometry for all packages of the same type, the laser and detector were firmly fixed in mounts. Supports were mounted for the packages as well, forcing each package to be positioned in a similar way in every measurement. The measurement series performed are summarized in Table 1.

### Table 1

Summary of the measurement series performed.

<table>
<thead>
<tr>
<th>Meas. No.</th>
<th>No. of pack.</th>
<th>Top material</th>
<th>Content</th>
<th>Detector</th>
<th>Gas sensed</th>
<th>Headspace atmosphere</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5</td>
<td>HDP white</td>
<td>Milk</td>
<td>PD</td>
<td>(O_2)</td>
<td>Air</td>
</tr>
<tr>
<td>2</td>
<td>6</td>
<td>LDP white</td>
<td>Milk</td>
<td>PD</td>
<td>(O_2)</td>
<td>Air</td>
</tr>
<tr>
<td>3</td>
<td>40(^*)</td>
<td>HDP white</td>
<td>Milk</td>
<td>PMT</td>
<td>(O_2)</td>
<td>(N_2)</td>
</tr>
<tr>
<td>4</td>
<td>100</td>
<td>HDP transp.</td>
<td>Juice</td>
<td>PD</td>
<td>(O_2)</td>
<td>(N_2)</td>
</tr>
<tr>
<td>5a</td>
<td>26</td>
<td>LDP white</td>
<td>Juice/water</td>
<td>PD</td>
<td>(O_2)</td>
<td>(O_2 + H_2O)</td>
</tr>
<tr>
<td>5b</td>
<td>1</td>
<td>LDP white</td>
<td>Juice/water</td>
<td>PD</td>
<td>(O_2)</td>
<td>(N_2)</td>
</tr>
</tbody>
</table>

\(^*\) GASMAS measurements were performed on 208 individual packages but reference sensor measurements on 40 of them.

Another laser system was used, as described in the corresponding section.

3. Results

3.1. Number of packages: 5; top material: white HDP; content: milk

The oxygen concentration of the headspace gas (air) in five packages containing milk was evaluated. The package model has a top made of white non-transparent HDP and a liquid volume of 1 l. The concentration was measured in the intact packages and, additionally, one of the packages was perforated and flushed with different nitrogen/oxygen mixtures to create a wider oxygen concentration range. With all measurements included, the difference in concentration result from the non-intrusive and intrusive techniques is at most 0.81% points of \(O_2\) while the residual standard deviation\(^2\), \(\sigma\), between the results from the two methods is 0.48% points.

3.2. Number of packages: 6; top material: white LDP; content: milk

The performance of GASMAS was further tested on six packages with a top made of white non-transparent LDP. The packages contained lactose free milk, packed in normal headspace atmosphere (air) and are available in Swedish retail stores. The \(O_2\) concentration of each package was measured first with the laser technique and then perforated and measured with the reference sensor. The results from these measurements are shown in Fig. 4. Since the oxygen concentration was very similar for all these packages, an additional package was perforated and its headspace filled with different nitrogen/oxygen mixtures to create a broader oxygen concentration range. With all measurements included, the difference in concentration result from the non-intrusive and intrusive techniques is at most 1.09% points while the residual standard deviation between the results from the two methods is 0.52% points.

To further reveal the potential of a non-intrusive technique a measurement series was also performed ‘continuously’ on a single package while the conditions inside changed. The system was set to repeatedly evaluate the concentration every tenth second while the package was first left at initial conditions (perforated package, ambient air conditions) until the package was first perforated and flushed, before it was sealed with a piece of tape and measured first with GASMAS and then with the reference sensor. This complete procedure was then repeated for several gas mixtures. The corresponding results are shown in Fig. 3. The difference in concentration result from the non-intrusive and intrusive techniques is at most 0.48% points.

\(1\) This assumes, e.g., that the filling is well controlled.

\(2\) The residual standard deviation is calculated as \(\sigma(c) = (\sigma_1^2/n_1 + \sigma_2^2/n_2)^{1/2}\), \(\Delta c\) is the sample vector, in our case being the residual of the concentration results obtained from the two techniques \((c_{\text{eval}} - c_{\text{cal}})\), \(n\) is the number of samples and is the mean of \(\Delta c\). As the concentrations in some of the measurements (not including the one presented in this section) cover only a small range, we have included the concentration zero in the results from the two techniques \((c = [0, c_{\text{eval}}]\) and \(c = [0, c_{\text{cal}}]\)).
flushed with pure nitrogen gas until \( t \approx 12 \text{ min} \). The package was then partly sealed, only leaving a small hole to allow for air to slowly diffuse in until about an hour had passed. Fig. 5 shows how the oxygen concentration is changing throughout the measurement series.

3.3. Number of packages: 40 (208); top material: white HDP; content: milk

These measurements were performed on 208 packages with a top made of white non-transparent HDP containing milk and with nitrogen flushed modified atmosphere. A subset of 40 packages was perforated and the oxygen concentration measured with the reference sensor, while the others were sent intact for other complementary analysis. The measurement results from the perforated subset are shown in Fig. 6. From this relatively large amount of data it can be concluded that the difference in concentration value from the non-intrusive and intrusive techniques is at most 1.4% points while the residual standard deviation is 0.65% points.

3.4. Number of packages: 100; top material: transparent HDP; content: orange juice

This series of measurements included 100 packages containing orange juice in nitrogen flushed modified atmosphere. The package top material was in this case transparent HDP, making the measurement situation a bit simplified due to the high light transmission of the material. However, since the plastic is somewhat diffuse, light scattering in the entrance and exit of the light beam passing the package is still strong and the path length therefore initially unknown. Fig. 7 shows the results of the evaluated concentration of oxygen by GASMAS and the reference sensor for each package in the order they were sampled. The vertical, black, dotted lines show the time events of changing the perforating needle and a filter in the reference sensor. (These changes need to be done now and then, as required by the reference sensor.) Two of these events were between the measurements of package 35 and 36, and between package 63 and 64, respectively. It is quite obvious how the reference sensor provides higher concentrations in general for packages measured between these two filter changes, and the suddenly larger residual (shown with red dots) of the two types of measurements can be expected to be connected with this. Another outlier is the measurement of package number 18.

In Fig. 8 the correlation between the results from the two measurement techniques is shown with measurements of packages 18 and 36–63 excluded. The difference in concentration result from the non-intrusive and intrusive techniques is at most 0.87% points while residual standard deviation is 0.30% points.

---

\[ \text{corr} = 0.999 \]

Fig. 3. Evaluated concentration against reference concentration for five individual imperforated packages of milk, shown with dots (blue). The crosses (red) represent measurements on a perforated package with different oxygen/nitrogen mixtures in the headspace. The correlation coefficient \(^3\) of the data from the two techniques is 0.999 (including point [0,0]). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

\[ \text{corr} = 0.997 \]

Fig. 4. Evaluated concentration against reference concentration for six individual imperforated packages of milk, shown with dots (blue). The crosses (red) represent measurements on a perforated package with different oxygen/nitrogen mixtures in the headspace. The correlation coefficient \(^3\) of the data from the two techniques is 0.997. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

\[ \text{corr} = 0.991 \]

Fig. 5. A 1 h measurement series during a time where the oxygen concentration was first decreased by flushing with pure nitrogen gas, after which ambient air was allowed to slowly seep in through a small hole. The exponential behavior of gas diffusion can be noticed.

\[ \text{corr} = 0.999 \]

from the non-intrusive and intrusive techniques is at most 1.4% points while the residual standard deviation is 0.65% points.

---

\[^3\] The correlation coefficient presented is the Pearson’s sample correlation coefficient calculated according to

\[
\text{corr}(c^{\text{eval}}, c^{\text{ref}}) = \frac{1}{(n-1)\sigma_{\text{eval}}\sigma_{\text{ref}}} \sum_{i=1}^{n} (c^{\text{eval}}_i - \bar{c}^{\text{eval}})(c^{\text{ref}}_i - \bar{c}^{\text{ref}})
\]

Here, \( c^{\text{eval}} \) and \( c^{\text{ref}} \) are the vectors of concentrations, \( \bar{c}^{\text{eval}} \) and \( \bar{c}^{\text{ref}} \) are the mean of the concentrations, and \( \sigma_{\text{eval}} \) and \( \sigma_{\text{ref}} \) are the standard deviations of the concentrations obtained by the non-intrusive technique and the reference sensor, respectively.
3.4.1. Number of packages: 26; top material: white LDP; content: water/juice

The final measurements were performed on a set of packages with package tops made of non-transparent, white, LDP. Some of the packages in this set contained orange juice while others contained pure water. The oxygen concentration in the package headspace was in general around 7–8% in the packages containing juice and around 15% in the ones containing water. In addition to the measurements on the 26 imperforated packages, one package (containing water) was perforated and the headspace filled with different nitrogen/oxygen mixtures to provide a few measurement points with other oxygen concentrations. The correlation between the reference sensor and GASMAS is shown in Fig. 9. The difference in concentration obtained by the two methods is here at most 3.0% points and the residual standard deviation 0.94% points.

As is clear from Fig. 9 the correlation is in general much worse for this set of measurements as compared to the previous measurements presented in this study. Further investigations showed that the uncertainty of these measurements is likely to be mostly present in the laser measurements but the cause is not completely known. In general, the largest uncertainty in the GASMAS measurements is the unknown path length and not the absorption fraction. The major influence on the path length is the optical geometry of the headspace which is affected by, e.g., differences in filling height. The effect of this geometric change seems to be larger for this measurement set. The filling precision regarding the volume of liquid in the package can often be controlled from the manufacturer depending on the present demands. A possible reason for the larger uncertainty in this measurement set can therefore be that the filling might have been less controlled than usual as the packages were not meant to be delivered to any customer. Another experience we have gained is that packages containing juice and water are more sensitive to changes in the optical geometry than those containing milk, since the stronger scattering from the milk surface helps to both increase the amount of light reaching the detector and to increase the average optical path length. The fact that the content was juice and water can therefore be another reason to the larger uncertainty found in the measurements for these packages. In the following section a tactic to circumvent the problems experienced with these packages is presented.

3.4.2. Dual-wavelength system to access unknown optical path lengths

One of our standard approaches to avoid uncertainties in sampled volume or path length is the use of an additional laser, simultaneously to the oxygen measurements sensing another gas of known concentration. If the concentration is well known the only unknown is the path length which therefore can be calculated from Eq. (1). By assuming the path lengths for the light sensing the two gases being the same the unknown path length in the oxygen measurement is determined. The gas with known concentration is in this case water vapor due to the fact that in smaller closed compartments with liquid water present the relative humidity is constant (for non-salt products the relative humidity can be assumed to be 100%) and the water vapor concentration can easily be obtained by knowing the temperature (Buck, 1996). The usefulness of this approach was therefore tested in a second experiment where it was investigated if the use of a pair of fiber coupled lasers for oxygen and water vapor (DFB, Nanoplus) could compensate for differences in the volume of liquid in the package (and thus for differences in headspace volume). The procedure was the following: one of the packages containing juice was perforated to assure ambient conditions with regards to oxygen concentration inside. Thirty five milliliters of juice were extracted and mixed with 35 ml of water. The package was then sealed with a piece of tape to let the relative humidity increase to 100%, something that occurs on a timescale of minutes at most. Both the oxygen sensing and water vapor sensing laser radiations were then sent into the package through the same optical fiber to sense as similar volume as possible. Five milliliters of the juice/water mixture were then added to the juice in the package and the measurement was performed again. This procedure was then repeated until the package content was 35 ml above the initial (nominal) level. The idea is that the ratio between the oxygen signal and the water vapor signal should be a better measure of the oxygen concentration than the oxygen signal standing alone. The result of the measurement series is shown in Fig. 10. Presented in the figure are the normalized path lengths (the mean is forced to be one) given by the sensed oxygen and water vapor together with their ratio. It is clear that the ratio is more independent of filling volume and should therefore be a better measure of the oxygen concentration. The standard deviation of the oxygen signal is here 0.13 and of the ratio 0.062 (corresponding to standard deviations of 1.0% and 0.5% points at a true oxygen concentration of 8%, respectively).
Fig. 10. Comparison between direct measurements of oxygen and the ratio of the oxygen signal and the water vapor signal as an evaluation of the oxygen concentration.

Table 2
Summary of the results from the measurement series. Column 5 shows the maximum difference in evaluated concentration between the reference sensor and the laser technique while column 6 shows the corresponding residual standard deviation. Column 7 shows the approximate transmission from laser to detector, i.e., the ratio between the power received by the detector and the power emitted by the laser.

| Meas. no. | No. of pack. | Top material | Content | max(|ΔcO₂|) | σ(ΔcO₂) | T (appr.) |
|----------|--------------|--------------|---------|-----------|----------|----------|
| 1        | 5            | HDP white    | Milk    | 0.81      | 0.48     | 5 × 10⁻⁶ |
| 2        | 6            | LDP white    | Milk    | 1.1       | 0.52     | 5 × 10⁻⁴ |
| 3        | 40           | HDP white    | Milk    | 1.4       | 0.65     | 1 × 10⁻⁵ |
| 4        | 100          | HDP transp.  | Juice   | 0.87      | 0.30     | 1 × 10⁻² |
| 5a       | 26           | LDP white    | Juice/water | 3.0       | 0.94     | 5 × 10⁻⁴ |

4. Final discussion and conclusions

We have presented experiments on a number of package types where we have investigated the oxygen concentration sensing performance of the diode laser spectroscopy technique GASMAS compared to a standard, intrusive, reference sensor. We can conclude that the non-intrusive method presented is performing well and shows good correlation with the reference method in general. Table 2 summarizes the results from the five measurement series along with an approximate value for the transmission from laser to detector (the ratio between the power received by the detector and the power emitted by the laser).

We chose to mainly go for the use of a single, non-fiber coupled, oxygen sensing laser, instead of two fiber connected lasers coupled into a common fiber: one sensing water vapor and one sensing oxygen. The dual-laser setup is otherwise something we implement in most situations when the path lengths differ substantially from one sample to another as is frequent in biological studies of, e.g., gas content in human sinus cavities (Persson et al., 2007). In those cases, there is no possibility to create a calibration as the one described in Section 2.2.1. and the path length needs to be obtained with the help of a water vapor sensing laser. It could, however, be beneficial to avoid such a system when it is not needed. The main reasons for this are the higher cost of using two lasers and the degraded system performance regarding other aspects than path length assessment, due to optical interference and lower output power related to the use of fibers.

The measurements of Fig. 5 suggest that also low oxygen concentrations are readily reachable with the spectroscopic technique. In general, the largest uncertainty in the measurements is the probed path length and not the measured absorption fraction. Thus, the relative accuracy at low gas concentrations (down to around one% point) is the same as the one at high concentrations. Exceptions can exist if the light transmission is extremely low, and the signal thus noisy. From an industrial perspective, measurements on head space gas, from low O₂ concentration to the one near ambient air are of all interest. This since gas-tight packages naturally is the preferred situation, but from a quality assurance perspective it is interesting to identify defective packages, that have for example “micro-pores” or other defects affecting the tightness. If they have that kind of deficiency they most likely have a gas composition that is near the one of ambient air, while packaging material that slowly permeate gases are interesting to study also at low O₂ concentrations. The results presented here suggest that a single laser system provides an oxygen concentration that in general lies within less than one% point away from the true concentration. For one of the measurement examples, we, however, notice that this difference is greater, but we also show that the measurement situation can be improved by the use of a dual-laser system when needed. It deserves to be mentioned that information about the probed path length could be obtained by estimating the headspace volume in other ways than with an additional laser. Examples of such ways can be the use of acoustic methods or simply weighing the package and measuring its volume.

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