

Deviations from Beer's Law in NDIR Gas Sensors

Non Dispersive InfraRed sensors function by monitoring the absorption of infrared radiation in the wavelength range affected by target gases, typically in the 3-5 micron wavelength range. Aliphatic hydrocarbons absorb in this region due to the fundamental C-H bond stretches and carbon dioxide absorbs in this region due to the fundamental asymmetric O=C=O stretch.

The fraction of radiation absorbed depends on the pathlength occupied by the target gas, the wavelength of radiation being measured and the molecule itself. The law of absorption, originally stated in 1729 in a memoir by P. Bouguer, was later rediscovered by Lambert and was expressed as:

$$-dl/l = b dx$$

where l is the intensity of radiation at a distance x from its entry into the medium and b is called the absorption coefficient. On integration with the boundary condition $l = l_0$ at $x=0$ we obtain:

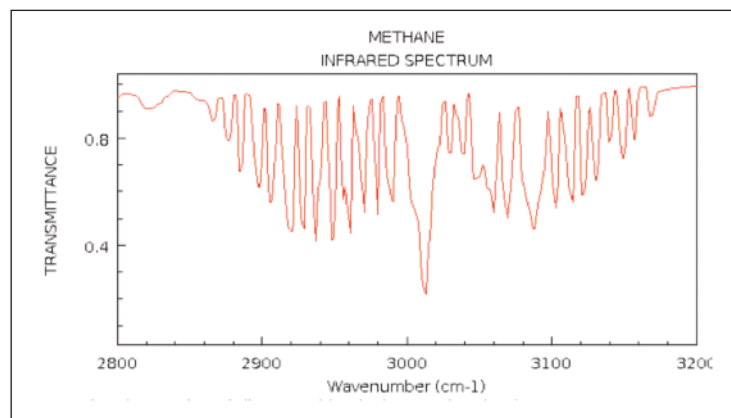
$$l = l_0 e^{-bx} \text{ and therefore } \ln(l/l_0) = \ln(T) = -bx$$

where T is known as the Transmittance. The preference for decadic logarithms in spectroscopy fields uses the definition $\log(l/l_0) = -ax$ where a is the (linear) absorption coefficient. In 1852, Beer showed, for many solutions of absorbing species in transparent media, that the coefficient a is proportional to the concentration of species c . Thus Beer's Law is:

$$\log(l/l_0) = -\epsilon cx$$

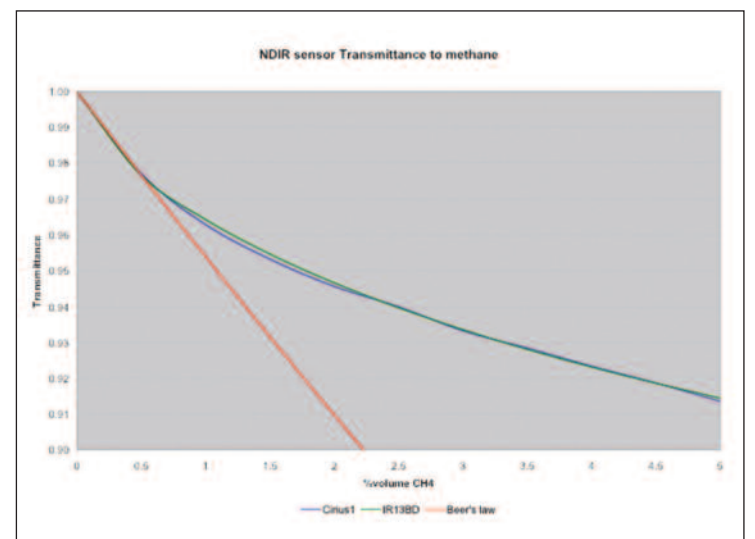
where c is the molar concentration, and ϵ is called the molar absorption coefficient or extinction coefficient. These absorption laws are the bases for various spectroscopic methods of analysis and are obeyed strictly only for monochromatic radiation. This is an important point in the discussion that follows.

What we are interested in measuring in the infrared region is absorption of radiation due to transitions in the vibration-rotation energy levels of target molecules. Such absorption only occurs if there is a change in dipole moment during these energy level transitions and therefore diatomic symmetric molecules such as H_2 , O_2 and Cl_2 display no absorption in the gaseous state. Other molecules have vibration-rotation spectra and absorb radiation in the infrared region. The absorption arises from transitions between definite rotational energy levels belonging to definite vibrational levels. These transitions occur when a photon of infrared radiation of the appropriate wavelength is absorbed and the selection rules for such transitions are defined as $\Delta V = \pm 1$ and $\Delta J = \pm 1$ for the corresponding vibrational and rotational levels. In certain cases (eg diatomic molecules with angular momentum about the internuclear axis such as NO) we can also have $\Delta J = 0$. So a vibration-rotation spectrum may display 3 branches where $\Delta V = \pm 1$ corresponding to the 3 cases $\Delta J = -1$ (P branch, lower energy, longer wavelength), $\Delta J = 0$ (Q branch) and $\Delta J = +1$ (R branch, higher energy, shorter wavelength). A good example is given by the infrared spectrum of methane shown below. The spectrum is somewhat complicated by combination bands but it does show the salient features of vibration-rotation spectra.:



In NDIR sensors we measure the intensity of a band of wavelengths and this band is defined largely by the bandpass of the optical filters fitted to the detectors. Typically a dual detector is used which has two active elements: One is fitted with a passband filter that allows radiation which

is not absorbed by target gases to pass and this forms a reference signal, the other is fitted with a passband filter that does allow radiation which is absorbed by target gases to pass. This forms the active signal and the intensity of radiation reduces as target gas concentration increases. The development of miniature plug in NDIR sensors, the first published UK sensor being described in 1998¹, has popularised the technique dramatically. The main problem is solving the requirement to achieve sufficient pathlength (in order to have sufficient sensitivity to gas) in such a restricted volume and all three independent UK sensor companies with NDIR technology based in Essex² have solved this problem in their own unique ways. Such sensors, in common with other miniature sensors from UK and overseas companies, demonstrate deviations from Beer's Law. This is not necessarily a problem and application notes relating to the first such sensor¹ derived an empirical relationship which is loosely based on Beer's Law; this relationship has been adopted by others. Typical examples of such deviations are shown in the Transmittance curves below for the Clairair Cirius1 sensor and the E2V Technologies IR13BD sensor (span values equalised) with them both compared to a Beer's law estimate based on matching the lowest concentration point:



The generally adopted empirical modification of the Beer's Law relationship is given by:

$$(1 - l/l_0) = S^*(1 - \exp(-\alpha * c^\beta))$$

where S is interpreted as the span of the sensor, c is the gas concentration and both α and β are constants dependent on the gas type and concentration units (%volume, %lel, ppm, etc). Clearly, if $S = 1$ and $\beta = 1$ this empirical relationship reduces to Beer's Law with α equating to ϵx . So what causes the deviations from Beer's Law? The methane spectrum gives us a clue, as does the Kubelka Monk theory³ which considered absorption, reflection and scattering.

Consider a passband optical filter intended for a hydrocarbon gas sensor, a typical example being a broad band filter with centre wavelength of 3008cm^{-1} (3.325 micron) and a HPBW of 160nm^4 . Now consider the methane spectrum above. It is clear that each individual wavelength within the range of the passband filter makes it's own contribution to the overall signal, effectively each wavelength has its own absorption coefficient (discussed above and designated ϵ). Some wavelengths have $\epsilon = 0$ as can be seen in the methane spectrum both between the vibration-rotation lines and beyond the range of the spectral plot. So what we see is a kind of integrated absorption coefficient over the passband range of the optical filter. If we also consider wavelengths that can be detected beyond the range of the passband filter (small out of band transmission through the filter caused by the substrate material) and angle of view effects then we have a combination of absorbed and unabsorbed wavelengths being detected together.

So we can consider that we have 2 intensities of infrared radiation being measured, I_a which is that which can be absorbed by the target gas (to varying degrees dependent on wavelength) and I_u which is that which is not absorbed by target gas. This modifies the Beer's Law

expression since $I = I_a + I_u$ and we assume I_u does not change with gas concentration. With the boundary condition $I_0 = I_a(0) + I_u$ and since we can only measure I and I_0 then if we assume I_u is a fixed percentage of I_0 and denoted by $I_u = \gamma I_0$ then we can modify the initial differential equation above to:

$$-dI/I = -dI/I_a = -dI/(I - \gamma I_0) = b dx.$$

On integration with the boundary condition $I = I_0$ at $x=0$ we now obtain:

$$(I - \gamma I_0) / (I_0 - \gamma I_0) = (I - \gamma I_0) / (I_0(1 - \gamma)) = e^{-bx}$$

This leads to:

$$I/I_0 = \gamma + (1 - \gamma)e^{-bx}$$

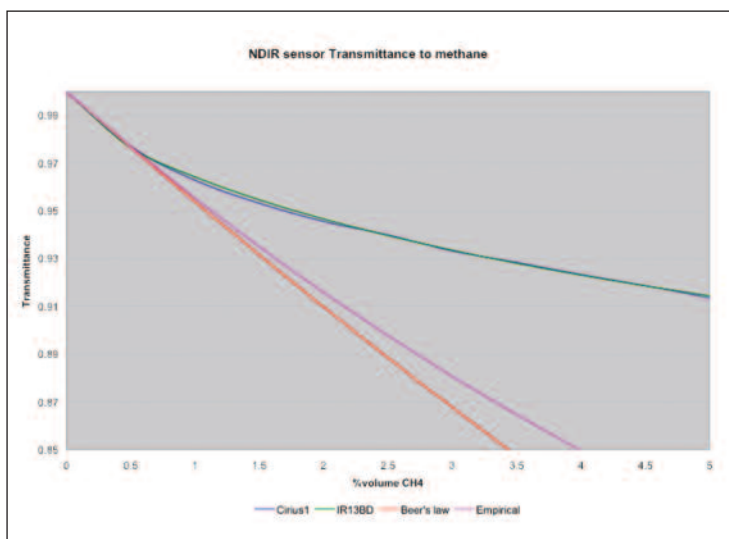
The percentage of absorbing radiation is therefore given by $(1 - \gamma)$ and this basically equates to the sensor span (denoted S above) for the given target gas (i.e. the maximum amount of radiation that can be absorbed) so we then have:

$$I/I_0 = 1 - S + Se^{-bx} = 1 - S(1 - e^{-bx})$$

And rearranging leads to the format of the empirical modification of Beer's law mentioned above but without a power term consideration:

$$(1 - I/I_0) = S(1 - \exp(-\alpha * c))$$

So we have deduced the basic theory behind the adopted empirical relationship and now we have to consider the power term effect. Without the power term we see the empirical transmittance curve bend away from the Beer's law curve in the observed direction but not by enough to explain the observed deviations fully as shown below:



So we need to consider the reason the power term appears. If we consider a miniature plug in sensor optic then by necessity the optic has to be folded in some way in order to achieve sufficient pathlength. This leads to the possibility of numerous alternative routes for radiation to reach the detector from the source, mainly through different internal reflections against internal optical structures. This in turn means that there are, in effect, a number of different pathlengths apparent in the sensor. In effect this leads to some distortion of the observed transmittance change since the longer pathlengths will make a larger contribution than the shorter pathlengths. Perhaps more important than this is the fact that the detector sees a passband of wavelengths and each wavelength has its own extinction coefficient. This means that the detector sees a summation of the effect of each individual wavelength within the passband of its optical filter. In addition, angle of view effects (especially changes in this effect with temperature) result in the detector seeing wavelengths that extend beyond the passband spectrum which is normally given at normal incidence. Therefore the intensity observed, $I = I_a + I_u$, can be modified in that I_a can be considered as a summation of individual intensities at individual wavelengths. Therefore we can consider:

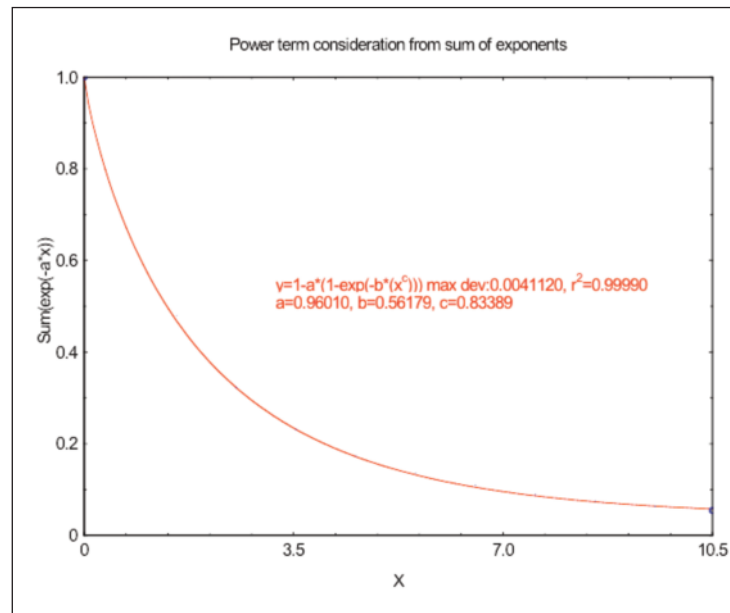
$$I_a = \sum (I_a)_\lambda$$

Where the summation covers the "active" absorbing wavelengths within the passband of the detector. Since Beer's Law strictly is obeyed by monochromatic radiation we can consider it as applying individually to each wavelength. As such the relationship between intensity and concentration observed by the detector becomes modified from $I=I_0 e^{-bx}$ by combining it with the summation to give:

$$I_a = \sum (I_0 e^{-bx})_\lambda$$

Where the extinction coefficient b has a unique value at every wavelength λ and therefore I_0 is also unique at each wavelength.

The problem is that we only measure the intensity so cannot separate the contribution of the extinction coefficient b from the contribution of the gas concentration x . It can be shown that if we consider a summation of exponents then we can derive a power term relationship. For example, if we simply sum 10 values of bx where b has values from 0.1 to 1.0 in 0.1 increments and x varies from 0 to 10.5 in 1.5 increments we can fit the data to a power term expression as shown below:

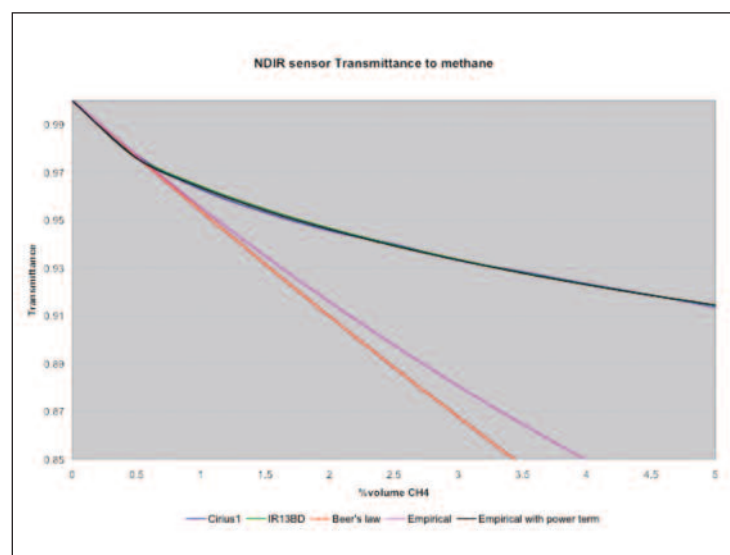


This tells us that the summation generates the same curve as a power term relationship where we have a constant exponential term and a power term is introduced into x . This shows that we can therefore consider the summation of individual Beer's Law components at individual wavelengths into a single passband related expression identical to the empirical expression above:

$$(1 - I/I_0) = S(1 - \exp(-\alpha * c^\beta))$$

So we can now explain both the exponential modification to Beer's Law and the power term within that modified expression whilst relating it back to Beer's Law itself.

If we apply it to the transmittance curves above we now get an extremely good fit to the data:



This expression is quite forgiving, small changes to the exponential constant and the power term do not have major effects on the curvature and so they allow transmittance curves to be fitted quite well. Changing the exponent and/or the power term gives fits to transmittance curves for different gases and this is useful where one finds general aliphatic hydrocarbon responses have similar curves since that allows one set of coefficients to be used for a number of target gases and the correlation is simply catered for in determining the span during calibration. A good example of the span contribution is when comparing the Clairair Cirius 2 CO₂ sensor with the Alphasense CO₂ sensor: They have quite similar power terms over the range 0-5% volume CO₂ but have quite different exponent and span values, the Alphasense sensor having a very high sensitivity due to the unique optical characteristics of that sensor. It is also interesting to note that at low concentrations the power term often reduces to the value 1.0, a typical example being a %volume carbon dioxide sensor over the ppm range; this is because the summation of the exponents does not cause a large distraction at low concentrations. This can also be seen in the above plots where for concentrations up to 0.5% volume methane we have Beer's Law, the empirical expression and the power term expression all giving good fits to the data.

We believe this is the first time the power term inclusion in the empirical expression has been mathematically explained.

AUTHOR DETAILS

Dr. Alan Doncaster,
C.Chem., M.R.S.C.,
Clairair Ltd,
Little Braxted Hall,
Witham Road, Little Braxted,
Witham, Essex,
CM8 3EU
Tel: +44 (0) 1376 516414
Fax: +44 (0) 1376 516415
Email: info@clairair.com



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