LINEAR TRANSFORMATION APPLIED TO THE CALIBRATION OF ANALYTES IN VARIOUS MATRICES USING A TOTAL HYDROCARBON (THC) ANALYZER

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KEYWORDS

ABSTRACT
Total hydrocarbon analyzers provide linear responses to methane and other hydrocarbons; however, the slope and intercept are dependent on the matrix. The matrix dependency requires that calibration be conducted for each matrix gas. The application of linear transformation (LT) enables a universal calibration performed in nitrogen matrix to be used for the analysis of analytes in various matrices.

INTRODUCTION
Purity analysis of specialty and industrial gases requires a variety of process instruments. These instruments include but are not limited to moisture, oxygen and total hydrocarbon (THC) analyzers. Automation can be used to save operator time and improve efficiency when performing impurity analysis on a series of gaseous samples. Most instruments used to perform portions of the assay of gases appear to have some sort of matrix effect.
In some cases, the presence of the matrix effect can be corrected by using a k factor derived from the sample flow rate. The k factor application allows the instruments to be calibrated in one matrix, and accurately analyze for impurities in a second matrix. For example, k factor is widely used by many instrument manufacturers in oxygen and moisture analyzers based on the electrochemical principle. Unfortunately not all instruments can have the matrix effect compensated for by use of the k factor. For instance, the total hydrocarbon analysis in a different matrix cannot be adjusted by applying a simple multiplier. The limitation constrains the possibility of automated laboratory analysis when a THC analyzer is used for analyzing samples in different matrices.

In cases where non-matrix correctable instruments are required to complete the analysis of several gases, they must be handled outside of the automation. The sequence of the analyses has to be suspended and the analyzer must be recalibrated for each successive change in matrix gas. Each calibration will generally require a minimum of two standards per matrix.

The interruption due to matrix effect makes automation of gas analysis inefficient. Using data acquisition software built in linear transformation capability removes the requirements for multiple calibrations during the sequence of analyses, thus enabling single calibration through a complete automation process.

**EXPERIMENTAL**

A Baseline Mocon Series 9000 Total Hydrocarbon analyzer was used to analyze methane concentration in various matrices. The analyzer is based on a flame ionization detector (FID) with Flow-Guard electronic control that delivers a small portion of the sample gas to the detector flame. During the combustion process, organic or hydrocarbon-based gases in the sample are ionized then they are detected by the instrument and reported as a concentration.

A gas mixture containing 40% of hydrogen and 60% of helium was used as fuel for the THC analyzer. Zero grade Air was used as a supportive gas for combustion. The detector analog output signals were in the range of 0-20 mA. The milliamp responses were converted to 0-10 volts using a 500 ohms resistor. The converted voltages were collected by an analog to digital (A/D) device manufactured by National Instruments. The A/D signals were processed by the data logger software developed by Applied Lab Automation Corporation.

Although any hydrocarbons could be used for this experiment, methane was selected for the analyte of interest due to the availability of NIST standards for comparison. Gas samples were prepared gravimetrically in high pressure cylinders. Methane with nominal values of 9.5 ppmv and 4 ppmv respectively was introduced to the cylinders containing a gas matrix of nitrogen, helium, or argon. The trans-filled cylinder with pure helium, argon, or nitrogen with
less than 0.1 ppm methane was used as a zero gas. The gas samples were regulated down to 30 psig and introduced to the THC analyzer via a 6-port Valco multi-position valve. The flow rate of the gas sample coming out from the multi-position valve was maintained constantly using a Cole-Palmer flow controller. The schematic diagram of the experimental set up is shown in Figure 1.

A gas sample containing methane in nitrogen matrix with nominal concentration of 9.5 ppm was used to span the THC analyzer. A research grade of N2 containing less than 0.1 ppm of methane was used to zero the response of THC analyzer. As soon as the span and zero steps were complete, a gas sample containing methane in nitrogen matrix with nominal concentration of 4.5 ppm was analyzed on the calibrated THC analyzer. The analyzer responses were plotted against the concentration of methane.

FIGURE 1. A SCHEMATIC DIAGRAM OF THE EXPERIMENTAL SET UP.

All operational parameters such as sample flow rate, fuel and air pressure of the detector were kept the same in the whole process. Without going through the above span and zero steps, the same THC analyzer was used directly to analyze argon and helium zero gases as well as sample gases containing methane with nominal concentrations of 9.5 ppm and 4 ppm in either argon or helium matrix.
RESULTS AND DISCUSSION

Table I shows the THC analyzer responses vs. concentrations of methane in various matrices. The THC analyzer was first calibrated with a span gas containing 9.50 ppmv of methane in nitrogen matrix. A research grade of nitrogen was confirmed to have less than 0.01 ppm of methane by GC-PDID. It was used to zero the THC response. Once the THC analyzer had completed the span and zero procedure, the following gases were analyzed: 4.00 ppmv methane in nitrogen, research grade helium, 9.50 ppmv methane in helium, 4.00 ppm methane in helium, research grade argon, 9.48 ppm methane in argon, and 4.01 ppmv methane in argon.

**TABLE I. THC ANALYZER RESPONSES VS. CONCENTRATIONS OF METHANE IN VARIOUS MATRICES.**

<table>
<thead>
<tr>
<th>SAMPLE NO.</th>
<th>METHANE CONC. (ppmv)</th>
<th>MATRIX</th>
<th>INSTRUMENT RESPONSE (volt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.00*</td>
<td>Nitrogen</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>9.50</td>
<td>Nitrogen</td>
<td>9.400</td>
</tr>
<tr>
<td>3</td>
<td>4.00</td>
<td>Nitrogen</td>
<td>4.113</td>
</tr>
<tr>
<td>4</td>
<td>0.00*</td>
<td>Helium</td>
<td>-0.114</td>
</tr>
<tr>
<td>5</td>
<td>9.50</td>
<td>Helium</td>
<td>6.196</td>
</tr>
<tr>
<td>6</td>
<td>4.00</td>
<td>Helium</td>
<td>2.545</td>
</tr>
<tr>
<td>7</td>
<td>0.00*</td>
<td>Argon</td>
<td>-0.459</td>
</tr>
<tr>
<td>8</td>
<td>9.48</td>
<td>Argon</td>
<td>7.767</td>
</tr>
<tr>
<td>9</td>
<td>4.01</td>
<td>Argon</td>
<td>3.488</td>
</tr>
</tbody>
</table>

*Methane was found to be less than 0.01 ppmv in all zero gases of research grade nitrogen, helium and argon.

Figure 2 illustrates the calibration curve of analyzer response vs. methane concentration in nitrogen matrix. The curve equation was generated by running a linear regression of three data points. Similarly, Figure 3 and Figure 4 demonstrate the calibration curves of methane in helium and argon matrices respectively. The equation of each calibration curve is shown below:

For methane in nitrogen matrix, the curve equation is:

\[ y = 0.9878x + 0.0594 \]  

(1)

Where \( x \) = concentration of methane in nitrogen matrix;

\[ y = \text{THC analyzer response at a given methane concentration in nitrogen matrix.} \]

With untreated data, the curve equation for methane in helium matrix is:
\[ y_1 = 0.6642x_1 - 0.1132 \quad (2) \]

Where \( x_1 \) = concentration of methane in helium matrix;
\( y_1 \) = THC analyzer response at a given methane concentration in helium matrix, and the analyzer was calibrated with methane standards in nitrogen matrix.

With untreated data, the curve equation for methane in argon matrix is:

\[ y_2 = 0.8627x_2 - 0.2806 \quad (3) \]

Where \( x_2 \) = concentration of methane in argon matrix;
\( y_2 \) = THC analyzer response at a given methane concentration in argon matrix, and the analyzer was calibrated with methane standards in nitrogen matrix.

![THC analyzer response vs. methane concentration in N2 matrix](image)

**FIGURE 2. THC ANALYZER RESPONSE VS. METHANE CONCENTRATION IN NITROGEN MATRIX.**
FIGURE 3. THC ANALYZER RESPONSE VS. METHANE CONCENTRATION IN HELIUM MATRIX.

![Graph showing THC analyzer response vs. methane concentration in He matrix.](image)

- Equation: $y = 0.6642x - 0.1132$
- $R^2 = 0.9999998$

FIGURE 4. THC ANALYZER RESPONSE VS. METHANE CONCENTRATION IN ARGON MATRIX.

![Graph showing THC analyzer response vs. methane concentration in argon matrix.](image)

- Equation: $y = 0.8627x - 0.2806$
- $R^2 = 0.9957$
It is obvious that each curve has a different slope and intercept. Without additional data treatment, it was essentially impossible to accurately analyze the methane concentration in helium or argon matrix if the THC analyzer was calibrated with methane standards prepared in nitrogen matrix.

Many laboratory instruments suffer discrepancies in analytical results based on factors associated with the matrix or the presence of contaminants. These phenomena were known to many instrument manufacturers and a list of correction factors could be applied to analysis manually when these effects were expected. On screen menu selectable correction factors are available for newer models of analyzers developed by the instrument manufacturers.

The simple multipliers could work well for some instruments, as in the case of diffusivity coefficient in trace oxygen analysis. However, matrix effects can be more complicated as found in THC analyzers requiring more advanced correction techniques than simple scalar multiplication. In the case of THC analyzer, the matrix effect is dependent upon the slope and intercept of a line equation corresponded to which matrix the analyte is suspended in.

In the case of THC analyzer, a proposed linear transformation technique [7] can be used to map the data from one calibration line to another. Methane was used as the example of analytes although any other hydrocarbons should work as well. The linear transformation from helium matrix to nitrogen matrix can be described in the following equation.

\[
y = ((x-b) \times m_{N2}/m) + b_{N2}
\]  

(4)

Where 
- \( y \) = concentration of methane in helium matrix;
- \( x \) = the THC analyzer response at a given methane concentration in helium matrix while the THC was calibrated with methane standards in nitrogen matrix;
- \( m \) = the slope of the methane curve in helium matrix;
- \( m_{N2} \) = the slope of the methane curve in nitrogen matrix;
- \( b_{N2} \) = the y axis intercept of the methane curve in nitrogen matrix;
- \( b \) = the y axis intercept of the methane curve in helium matrix.

If the values of \( m_{N2}, m, b, \) and \( b_{N2} \) are plug in with the information from equations (1) and (2), the equation (4) can be re-written as follows:

\[
y = ((x + 0.1132) \times 1.4872) + 0.0594
\]  

(5)

The equation (5) can be re-arranged as follows:

\[
y = 1.4872x + 0.2269
\]  

(6)
Equation (6) was used as a conversion tool that allows the methane concentration in helium matrix to be analyzed accurately using the same THC analyzer calibrated with the methane standards prepared in nitrogen matrix. The same logic can be applied to derive a relationship as shown in equation (7) for analyzing methane concentration in argon matrix using the same THC analyzer calibrated with methane standards prepared in nitrogen matrix.

\[ y_a = 1.1450x_n + 0.3807 \]  

Where \( y_a \) = concentration of methane in argon matrix;

\( x_n \) = the THC analyzer response at a given methane concentration in argon matrix while the THC was calibrated with methane standards in nitrogen matrix;

### TABLE II. DEMONSTRATION OF THE LINEAR TRANSFORMATION TECHNIQUE APPLIED TO A THC ANALYZER WHEN THE ANALYSES WERE INVOLVED WITH SAMPLES IN MULTIPLE MATRICES.

<table>
<thead>
<tr>
<th>METHANE CONC. (ppm)</th>
<th>N2 MATRIX THC CURVE RESPONSE(^a) (volt)</th>
<th>HE MATRIX THC CURVE RESPONSE(^b) (volt)</th>
<th>HE MATRIX THC CURVE RESPONSE(^c) WITH LT</th>
<th>AR MATRIX THC CURVE RESPONSE(^d) (volt)</th>
<th>AR MATRIX THC CURVE RESPONSE(^e) WITH LT</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.0594</td>
<td>-0.1132</td>
<td>0.0594</td>
<td>-0.2806</td>
<td>0.0594</td>
</tr>
<tr>
<td>1</td>
<td>1.0474</td>
<td>0.5510</td>
<td>1.0472</td>
<td>0.5821</td>
<td>1.0472</td>
</tr>
<tr>
<td>2</td>
<td>2.0350</td>
<td>1.2152</td>
<td>2.0350</td>
<td>1.4448</td>
<td>2.0350</td>
</tr>
<tr>
<td>3</td>
<td>3.0228</td>
<td>1.8794</td>
<td>3.0228</td>
<td>2.3075</td>
<td>3.0228</td>
</tr>
<tr>
<td>4</td>
<td>4.0106</td>
<td>2.5436</td>
<td>4.0106</td>
<td>3.1702</td>
<td>4.0106</td>
</tr>
<tr>
<td>5</td>
<td>4.9984</td>
<td>3.2078</td>
<td>4.9984</td>
<td>4.0329</td>
<td>4.9984</td>
</tr>
<tr>
<td>6</td>
<td>5.9862</td>
<td>3.8720</td>
<td>5.9862</td>
<td>4.8956</td>
<td>5.9862</td>
</tr>
<tr>
<td>7</td>
<td>6.9740</td>
<td>4.5362</td>
<td>6.9740</td>
<td>5.7583</td>
<td>6.9740</td>
</tr>
</tbody>
</table>

\(^a\)Curve equation of THC analyzer response vs. methane concentration in nitrogen matrix: \( y = 0.9878x + 0.0594 \).

\(^b\)Curve equation of THC analyzer response vs. methane concentration in helium matrix: \( y = 0.6642x - 0.1132 \). The analyzer was calibrated with methane standards in nitrogen matrix.

\(^c\)Adjusted methane concentration in helium matrix by linear transformation using the equation \( y = 1.4872x + 0.2269 \), where \( x \) is the analyzer response of methane in helium matrix and the analyzer was calibrated with methane standards in nitrogen matrix.
Curve equation of THC analyzer response vs. methane concentration in argon matrix: $y = 0.8627x - 0.2806$. The analyzer was calibrated with methane standards in nitrogen matrix.

Adjusted methane concentration in argon matrix by linear transformation using the equation $y = 1.1450x + 0.3807$, where $x$ is the analyzer response of methane in argon matrix and the THC was calibrated with methane standards in nitrogen matrix.

The transformation from one curve in helium matrix to the other in nitrogen matrix was accomplished within the data logger software. The instrument responses to methane concentrations were mapped from one matrix to the other using the linear transformation function provided in the data logger software. Table II demonstrates the linear transformation technique applied to the THC analyzer when the analyses were involved with samples in multiple matrices.

Once the conversion curve was input to the data logger software, the samples in helium or argon matrix were analyzed again to confirm the feasibility of this approach. Table III shows the analytical results from THC analyzer without corrections as well as the results from the data logger software with built-in linear transformation function. It clearly shows a great improvement in analytical accuracy by using the linear transformation technique when the THC analyzer was utilized to determine the concentration of an analyte in various matrices. As shown in Table III, the adjusted analytical values for methane in helium matrix agreed with the blended methane concentrations with less than 2% difference even if the THC analyzer was calibrated only with methane standards prepared in nitrogen matrix. The disagreement was slightly higher at around 5% when the matrix was argon. With more data points included in the calibration, the disagreement is expected to be minimized.

<table>
<thead>
<tr>
<th>SAMPLE NO.</th>
<th>METHANE CONC. (PPM)</th>
<th>MATRIX</th>
<th>INSTRUMENT READING (ppm)</th>
<th>ADJUSTED* READING (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.00</td>
<td>Helium</td>
<td>2.55</td>
<td>3.97</td>
</tr>
<tr>
<td>2</td>
<td>9.50</td>
<td>Helium</td>
<td>6.20</td>
<td>9.63</td>
</tr>
<tr>
<td>3</td>
<td>4.01</td>
<td>Argon</td>
<td>3.33</td>
<td>4.17</td>
</tr>
<tr>
<td>4</td>
<td>9.48</td>
<td>Argon</td>
<td>7.77</td>
<td>9.01</td>
</tr>
</tbody>
</table>

*Adjustment was based on the derived equations (6) and (7). Adjustment was accomplished within the data logger software.
CONCLUSIONS

The application of linear transformation was confirmed to be able to generate a universal calibration performed in nitrogen matrix to be used for the analysis of analytes in various matrices. This is a valuable tool when the analyses of analytes are in various matrices and size of test samples is large. Automation of analyses involving multiple matrices can be achieved even if a matrix dependent analyzer such as THC analyzer is used. Although this paper mainly discussed the application used for a THC analyzer behaving linear responses, it could also be applied to a non-linear instrument as long as the relationship of responses in various matrices can be established experimentally.
REFERENCES


