IMPROVED CALIBRATION AND OPERATION OF A STABLE-GAS QUANTIFICATION MANIFOLD AS PART OF A RADIOXENON COLLECTION SYSTEM

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ABSTRACT

Radioxenon detection as part of the Nuclear Explosion Monitoring program involves measuring the ratio of the radioactive Xe isotopes (^{135}Xe, ^{133}Xe, ^{131m}Xe and ^{133m}Xe) to the stable (non-radioactive) isotopic abundance. Pacific Northwest National Laboratory currently uses a thermal conductivity detector (TCD) to measure the stable xenon gas composition immediately after the nuclear measurement is complete on their automated radionuclide samplers. When combined with absolute pressure, temperature and volume, the total volume of stable xenon (cubic centimeters of xenon at standard temperature and pressure) collected can be calculated and the quantity of radioxenon per volume of air is derived. A commercial TCD is a reliable device for measuring percent composition of binary mixtures provided the pressure of the sample is at or near atmospheric pressure; under these conditions the thermal conductivity of the sample is independent of pressure. However, at low sample pressures a pressure-dependent term begins to influence the thermal conductivity of the gas sample and needs to be accounted for if reliable results are to be obtained. To establish a means of correcting for the pressure effect, several blended gas mixtures (xenon in nitrogen) were analyzed over a wide range of pressures (10–760 Torr) on a test manifold fitted with a commercial TCD. These data were then analyzed and an automated calibration algorithm established and used to correct for the pressure effect in the raw TCD readings. The currently implemented routine uses the absolute pressure measurement to “look-up” the necessary calibration coefficients, which are used for TCD pressure normalization. It is estimated that this technique allows the use of TCD instruments to measure binary mixtures reliably down to a pressure of 10 Torr, much lower than is currently achievable with these devices. These results and an in-depth discussion of the pressure compensation approach will be reviewed in this paper.

OBJECTIVES

The objective of this work is to establish and demonstrate a technique for removing the pressure dependence from percent composition measurements of a binary gas taken with a commercial TCD. It is shown that this approach improves the accuracy of the measured percent xenon in nitrogen in low pressure gas samples compared with conventional approaches, positively impacting the error budget in radioxenon measurements.

A TCD is a simple device used for measuring the percent composition of a binary gas mixture. Such a measurement is an important part of the stable gas measurement (along with temperature, pressure and volume) and is usually performed after the activity of a xenon gas sample is determined by a nuclear counting measurement (Hayes et al., 1999). Binary gas mixtures are often encountered in radioxenon measurements due to the presence of a carrier gas (e.g., nitrogen or helium) used in the chromatographic isolation of the xenon sample. A typical TCD operates by measuring the power dissipated by a heated wire placed in the gas sample itself (Jitschin and Ruschitzka, 1993). Gas mixtures with a higher thermal conductivity remove more heat from the wire than gases with low thermal conductivity. Compositional analysis of the binary mixture is achieved by comparing the measured power dissipated against a 2-point calibration employing pure samples of the two gases.

The thermal conductivity of a gaseous mixture is a function of many parameters and is nontrivial to calculate. One very important aspect of the thermal conductivity of gases is its invariance to pressure at 1 atmosphere and above. Due to the gas dynamics that govern thermal conductivity, terms involving pressure cancel at these higher pressures. Therefore, all commercially available TCDs are specified for operation at or very near atmospheric pressure. A problem arises when these sensors are used at lower pressures because the thermal conductivity of the gas depends on both the intrinsic properties of the gas, as well as, the pressure of the gas. In many applications where compositional analysis is required, the pressure of the sample may be well below 1 atm (or 760 Torr) introducing significant accuracy errors. Because of this a study was performed to determine the feasibility of pressure compensating TCD readings from xenon/nitrogen gas mixtures over a range of pressures from 10 to 760 Torr.

RESEARCH ACCOMPLISHED

For this study a simple apparatus was assembled consisting of a commercially available TCD unit (HiTech Instruments, model K1550), an absolute pressure transducer (MKS Instruments, 1000-Torr capacitance manometer) and a secondary binary gas analyzer based on an acoustic measurement (Lorex Industries, Piezocon). These units were connected to a small leak tight manifold that could be evacuated to < 100 m Torr. Certified gas mixtures were purchased from 20%, 40%, 60%, 80%, and 95% xenon in nitrogen, in addition to standard purity nitrogen and xenon gases. The Piezocon sensor from Lorex industries was used to accurately and precisely measure the “true” composition of the purchased mixtures. The Piezocon has a rated accuracy of better than 0.1% for xenon/nitrogen mixtures. The HiTech TCD was calibrated using pure nitrogen and xenon carefully following the manufacturer’s instructions.

The procedure for a typical measurement involved evacuating the manifold to the base pressure and flushing with the gas mixture to be tested; this was repeated 3 times. The gas mixture was then added to the manifold to a pressure of 800 torr. The pressure, TCD value and Piezocon reading were all recorded. The pressure in the manifold was then reduced to the next target value by slightly opening a valve connected to the vacuum pump. The three readings were recorded and the pressure reduced again down to a lower limit of 2.5 Torr. This entire process was repeated 3 times to check for consistency and to provide for average sensor readings (with an estimate of error). Once the measurements for one mixture were complete, the cylinder was exchanged, the manifold flushed, and the series of 3 measurements were repeated. One additional mixture was created in the manifold by adding pure xenon to pure nitrogen already in the manifold and using their partial pressures to establish the percent composition (5.4% xenon in nitrogen) at a final pressure of 760 torr. Thorough mixing of this custom blend was verified by monitoring the Piezocon’s output over 24 hours. After approximately 16 hours the gases were sufficiently mixed for the measurement to begin. Only one series of measurements for this mixture was performed (instead of the 3 for the other gases). All measurements were performed near room temperature.

Pressure-dependent TCD data obtained for the 40% xenon in nitrogen mixture is shown in Figure 1. As mentioned previously, an accurate measurement of the percent composition is simultaneously obtained using a commercial acoustic sensor (Piezocon from Lorex Industries) for pressures > 75 Torr (the Piezocon stops responding below this pressure). The acoustic sensor has much higher precision and accuracy compared with the TCD; however, it suffers from a larger internal volume and a minimum operating pressure of 75 Torr, making it unsuitable for many applications where a limited amount of sample is available for analysis. Two notable observations about the pressure dependence of the TCD can be made from Figure 1. A large offset between the TCD and the acoustic sensor is present at atmospheric pressure where the TCD instrument is specified to operate. Also shown in Figure 1 is the impact of pressure on the TCD reading itself, which is a minor effect at higher pressure but becomes significant at pressures below 200 Torr.

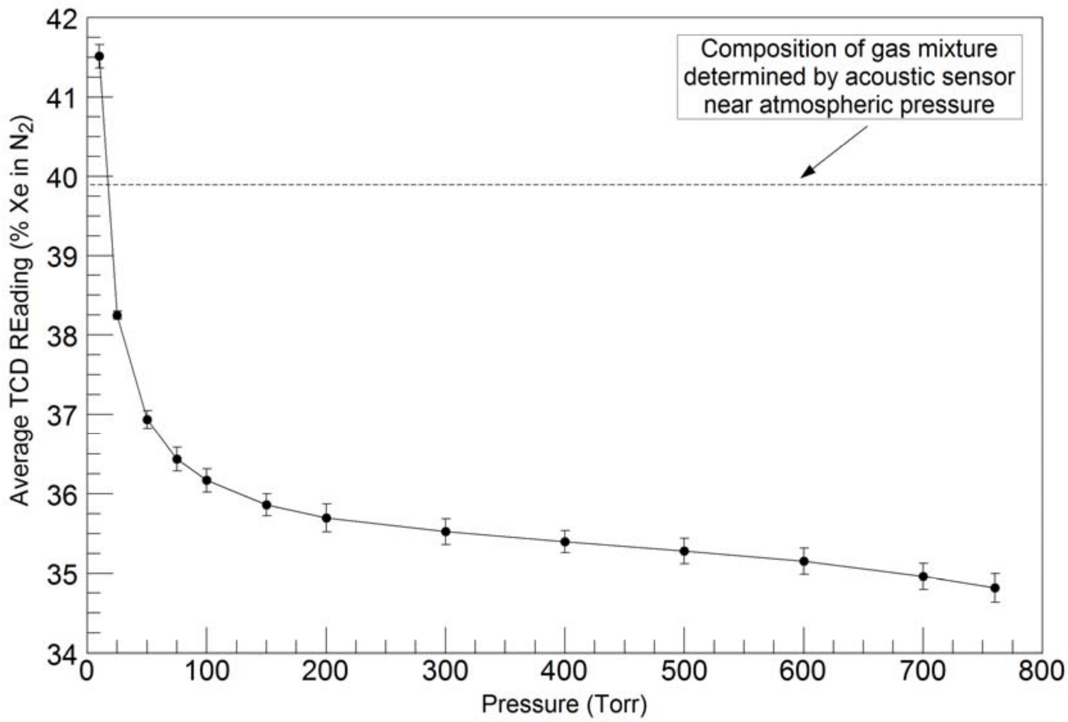

Figure 1. TCD readings as a function of pressure for a specific Xe/N_2 mixture (39.9%). The error bars represent 1 standard deviation of the 3 runs performed for this mixture.

Figure 2 shows the TCD reading as a function of pressure for all the gas mixtures used in this study. All traces show similar pressure dependence to that shown in Figure 1. The TCD readings for the low-pressure 100% xenon samples are artificially clamped or saturated at 100% since the instrument is not designed to output signals above 100%. The offset between the TCD instrument and the acoustic sensor at 760 Torr varies considerably and is largest for mid-range percent compositions.

Compensation Approach

The strategy for compensating the TCD reading involves determining an empirical relationship between "true" percent composition and measured percent composition for a wide range of mixtures and pressures. This is done by first interpolating the data in figure 2 along the pressure coordinate to yield a grid resolution of 1 Torr. The curves are all smoothly varying; therefore, the interpolation step is not likely to add significant error. Once the interpolation step is complete the "true" versus measured percent composition for each pressure is fit with a 5^{th} order polynomial. The coefficients from the fitting process for each pressure along the 1 Torr grid are stored. Three of these curves are plotted in Figure 3 along with their corresponding polynomial fit for 10, 200 and 760 Torr.

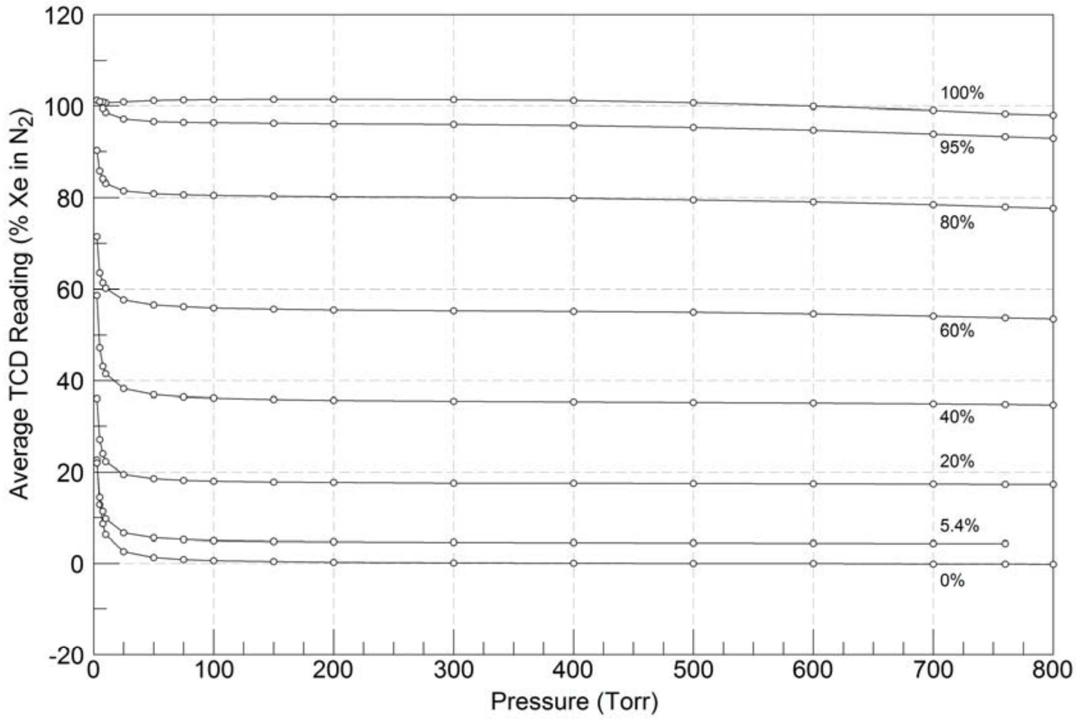

Figure 2. Pressure dependence of TCD compositional analysis as a function of sample pressure for all mixtures of xenon in nitrogen used in this study. Open circles are measured data, solid lines are interpolated data on a 1-Torr grid. Actual %Xe values are inserted for comparison.

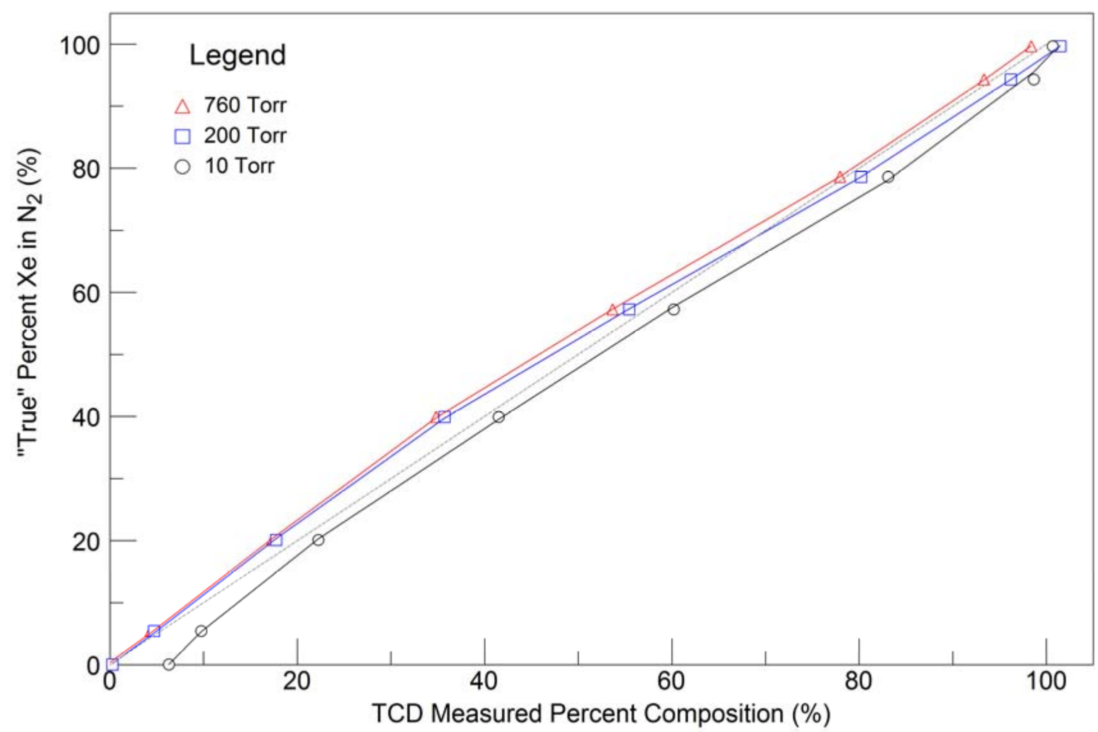

Figure 3. Actual versus measured percent composition for various xenon/nitrogen mixtures at three different pressures (760, 200, and 10 Torr), along with their corresponding 5th order polynomial fits. A dashed gray line with a slope of 1 is shown for reference.

Using this approach the previously measured TCD readings (shown in Figure 2) were used to generate a full set of coefficients for the 13 different pressures selected for this work. These polynomial coefficients are listed in Table 1. In the final form the matrix is much larger, with pressure resolution of 1 Torr.

Table 1: Polynomial values used in the compensation equation for the different pressures measured in this work.

	Polynomial Coefficients					
Pres. (Torr)	**a0**	**a1**	**a2**	**a3**	**a4**	**a5**
10	-11.72989	2.1644216	-0.0523550	0.0011240	-1.160E-05	4.479E-08
25	-3.426932	1.3785450	-0.0111410	0.0001835	-2.080E-06	9.966E-09
50	-1.355051	1.1667738	0.0026191	-0.0001701	1.767E-06	-4.985E-09
75	-0.785500	1.1193978	0.0062028	-0.0002692	2.889E-06	-9.469E-09
100	-0.480391	1.0955389	0.0080529	-0.0003210	3.483E-06	-1.188E-08
150	-0.227057	1.0760084	0.0098273	-0.0003729	4.091E-06	-1.436E-08
200	-0.061589	1.0536303	0.0114900	-0.0004161	4.554E-06	-1.613E-08
300	0.078753	1.0448359	0.0124288	-0.0004452	4.905E-06	-1.759E-08
400	0.150177	1.0419728	0.0127096	-0.0004522	4.980E-06	-1.787E-08
500	0.225328	1.0346178	0.0133195	-0.0004682	5.163E-06	-1.860E-08
600	0.282149	1.0385274	0.0128814	-0.0004497	4.908E-06	-1.743E-08
700	0.355955	1.0286183	0.0136278	-0.0004636	5.029E-06	-1.781E-08
760	0.358801	1.0425580	0.0124370	-0.0004211	4.470E-06	-1.530E-08

Implementation and Testing

When measuring an unknown mixture, the TCD reading and absolute pressure are recorded. The pressure value is used to “look-up” the correct coefficients for the polynomial expression, which also contains the raw TCD reading; for example at 200 Torr the expression is,

$$\begin{aligned}\%_{Xe/N2}\left(@\,200\,Torr\right) &= -0.06158+1.0536\left(\%_{TCD}\right)+0.01149\left(\%_{TCD}\right)^2 \\ &\quad -4.1616\times10^{-4}\left(\%_{TCD}\right)^3+4.5534\times10^{-6}\left(\%_{TCD}\right)^4-1.6131\times10^{-8}\left(\%_{TCD}\right)^5 .\end{aligned} \tag{1}$$

A software routine was written incorporating the polynomial coefficients and communication protocol for the TCD unit and the pressure transducer. The routine records the raw TCD reading and pressure and returns the compensated TCD value. To test the overall approach, the original raw TCD and pressure measurements were used as input to the software routine. The compensated TCD output data are plotted in Figure 4, along with the raw TCD measurements and indications of the actual mixture composition. As can be seen in Figure 4, the compensated TCD values are nearly independent of pressure (except at the lowest pressures measured) and the offsets are removed. A comparison of the relative accuracy errors between the raw and compensated TCD values is shown in Figure 5a and 5b, respectively. The relative accuracy error is defined as

$$rel.\,error(\%) = \left[\frac{\left(TCD\left(\%Xe\right)-Actual\left(\%Xe\right)\right)}{Actual\left(\%Xe\right)}\right]\times100\% \tag{2}$$

where the Actual (%Xe) value is that value measured by the acoustic sensor at 760 Torr. The relative errors include the calibration offset error in addition to the pressure effect. The compensated errors are all within +/- 1.0% down to 10 Torr, with the exception of the 5.4% xenon sample. The relative errors on the 0% xenon sample are extremely large simply because of the way relative errors are calculated in Equation. 2 with the “true” value in the denominator (which in essentially zero) and therefore are not shown. For the lowest percent composition sample (5.4% xenon), the absolute error in the compensated results is on the order of 0.1 – 0.3%. It is worth noting that for samples consisting of greater than 50% xenon in nitrogen, the total relative error (in the raw TCD readings) down to 10 Torr is typically less than +/- 5%.

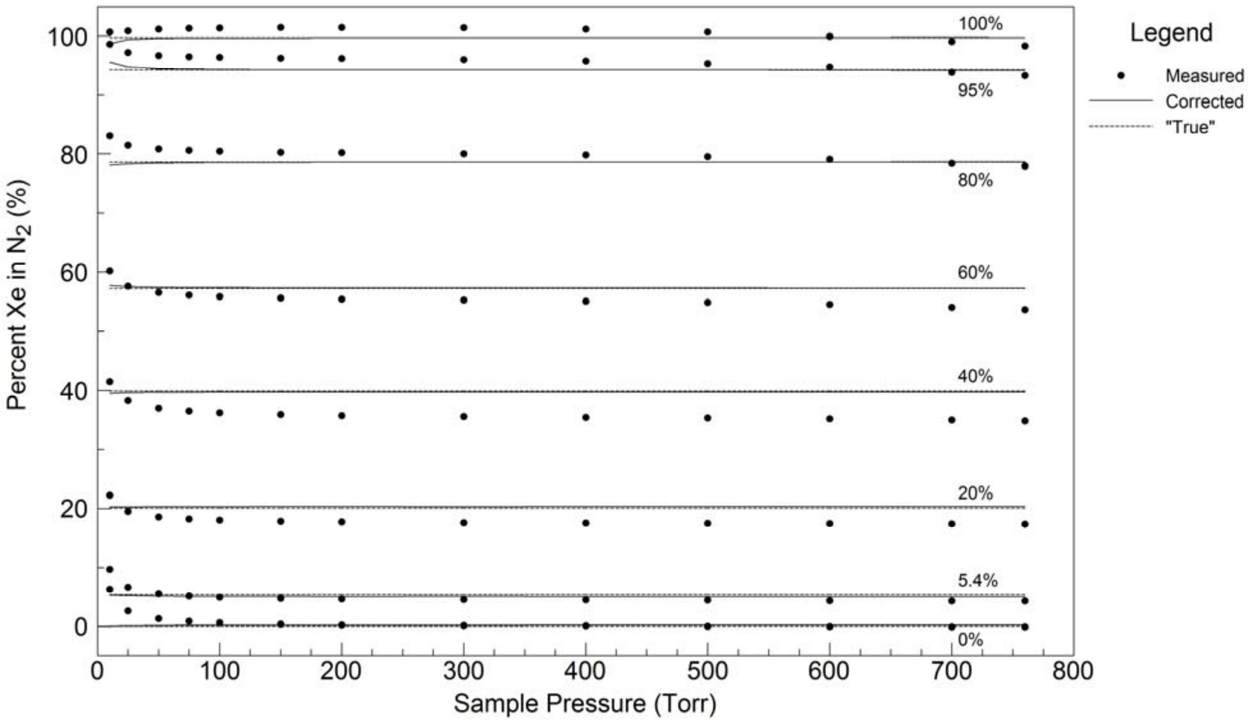

Figure 4: Comparison of raw TCD readings (dark circles), compensated readings (solid lines) and true values (dashed lines) for all the mixtures over the pressure range (10-760 Torr). The compensation removes both the pressure effect and the calibration offset error.

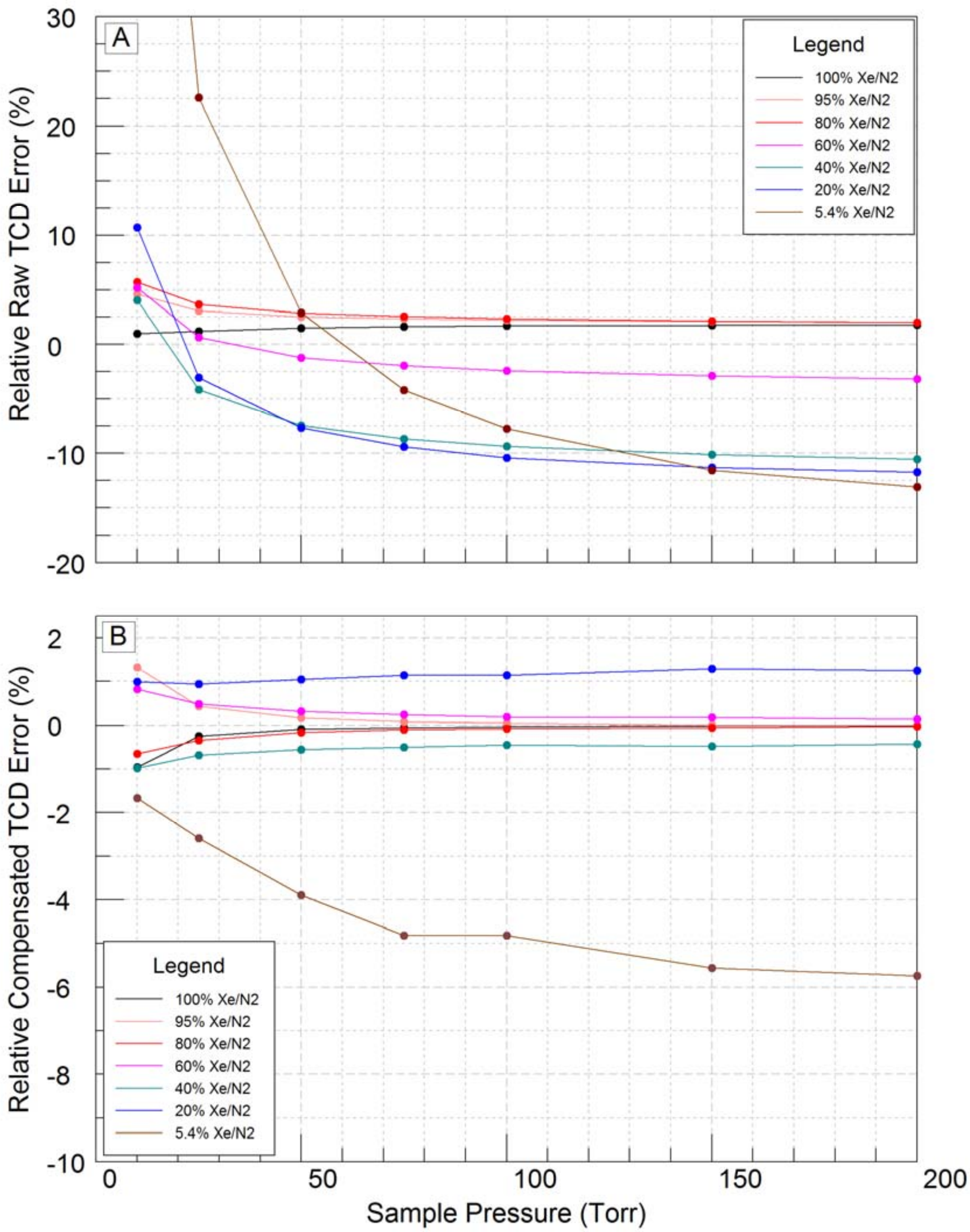

Figure 5. The relative accuracy error of the raw (uncompensated) TCD values as a function of pressure and composition is shown in the upper plot (5a). The relative accuracy error of the compensated TCD values is shown in 5b.

CONCLUSIONS AND RECOMMENDATIONS

It was shown that by carefully measuring the output of a thermal conductivity detector as a function of both percent composition of a binary mixture and absolute pressure, a calibration routine can be developed that extends the useful range of a standard TCD down to pressures of 10 Torr, with relative accuracy errors <1% for mixtures containing greater than 5-10% xenon in nitrogen. This approach allows for the use of standard TCD units in the accurate determination of % xenon in nitrogen in low-pressure gas samples, which have also been analyzed for radioxenon by nuclear methods.

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