Altamira Note
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Calibration of AMI Instruments for Determination of Loop Size, Dead Volume, and Temperature Calibration

INTRODUCTION

Calibration procedures are extremely important in order to obtain meaningful results that can be systematically reproduced over time and compared with results obtained using other instrumentation. This *Altamira Note* describes some routine techniques that can be used to calibrate the sample loop and to ascertain that the temperature read-back is correct.

PULSE LOOP CALIBRATION BY DIRECT INJECTION

This method provides the fastest and most direct route to calibrating the pulse loop and it is the one used at Altamira Instruments to calibrate the pulse loop of every instrument. It involves pulsing a marker gas into a carrier gas using the pulse loop and comparing the obtained area with that of a manual injection of the same gases using a gas-tight syringe. The advantage of this method is that it is fairly fast and several measurements can be taken in a relatively short period of time in order to average out random errors. However, it does suffer from several deficiencies, such as: (1) the accuracy of the gas syringe is unknown; (2) syringe leakage may occur between filling and injecting, changing the composition of the marker gas; (3) it is an entirely manual operation and thus may be operator-dependent. However, some of these deficiencies can be minimized. For example, air can be used as the marker gas thus minimizing the effect of leakage.
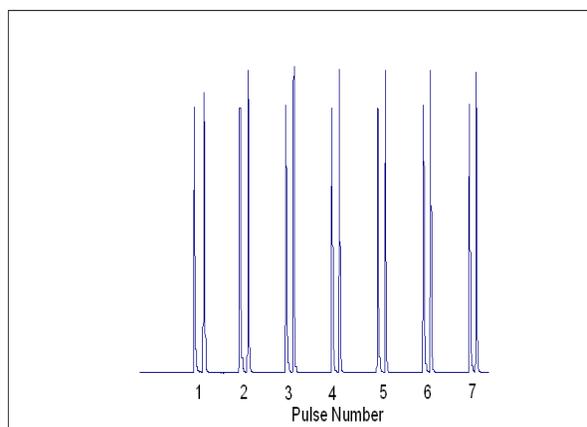

Figure 1. Pulse loop calibration by injection. Each pair of pulses represents a pulse from the pulse loop followed by a pulse from a manual injection, respectively.

In practice, an automated experiment is set up which consists of a pulse calibration procedure with several pulses and a long enough data collection period so that after each automatic pulse is complete there is enough time for a manual injection through the septum port. Figure 1 shows a typical calibration experiment. Seven pulses are delivered via the pulse loop, each followed by injection of a (nominally) 500 µL aliquot. The areas of the pulse-loop injections and the syringe-injections are obtained using the analysis feature of the Altamira software and the volume of the pulse loop calculated. Table 1 shows the results for this particular experiment.

TABLE 1

Summary of the integrated areas from Figure 1

Pulse Number	Integrated Pulse Area, counts	Integrated Injection Area, counts	Calculated Pulse Loop Volume, μL
1	7411	7600	488
2	7464	7363	513
3	7416	7380	502
4	7477	7317	511
5	7444	7307	509
6	7419	7264	511
7	7463	7287	512

ave $= 507 \pm 9$ μL

This calculated volume of 507 μL is typical for a nominally 500 μL loop.

PULSE LOOP CALIBRATION BY
EXTERNAL STANDARD

An alternative method of calibrating the pulse loop is to perform a TPR on a standard sample of known composition and known reducibility. This would have the advantage of not requiring constant operator intervention during the experiment. One possibility is to use a pure oxide of an easily reducible metal, such as copper (II) oxide, CuO.

A series of TPR experiments were performed on different loadings of samples of CuO. The TPR was conducted using a calibrated 10% H_2/Ar mixture. The sample was ramped from 50°C to 550°C at 10^0C/minute. The water produced during TPR was collected in the trap which was chilled using an isopropanol-liquid nitrogen slurry. CuO samples ranging from 0.028 g to 0.199 g were used.

A typical TPR pattern is shown in Figure 2. As can be seen, the reduction trace is quite asymmetric and broad. This is likely due to the relatively large size of the CuO particles.

The reduction trace can be integrated and its percent reduction calculated based on the loop volume determined by direct injection. Based on the determined value a loop volume can be calculated based on 100% reduction. These results are shown in Table 2 for a series of measurements using different sample weights.
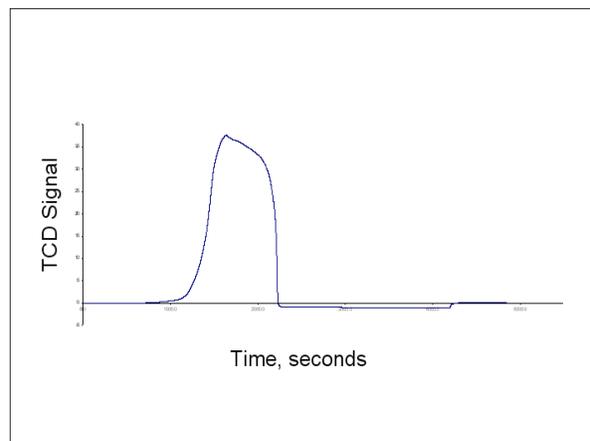

Figure 2. Reduction of 0.101 grams of CuO by TPR.

TABLE 2

Calculated percent reduction and loop volume using CuO as an external standard

Sample weight, g	% Reduction, calculated using 509 µL loop	Recalculated Loop Volume, µL
0.028	102	497
0.055	114	444
0.105	120	422
0.199	125	405

As can be noted, the higher the sample weight the lower the percent reduction calculated. Only the sample with the lowest weight gave reasonable results. However, in all cases the sample after reduction was of a characteristic copper color and appeared to be 100% reduced. The low and varying reduction numbers are likely due to poor integration of the asymmetric signal. Thus we conclude that the use of pure copper oxide as an external standard is not suitable for calibration.

A different and perhaps better choice for an external standard would be an easily reducible catalyst. Nickel oxide on silica is know to reduce easily (1) and may thus serve as an external standard.

A commercially available nickel on silica (Strem Chemicals #28-1900) was evaluated as a calibration external standard. The material, as supplied, is listed as 64% reduced nickel which corresponds to 69% by weight NiO after calcination in air (2). The same TPR procedure was used as detailed above for the CuO.

Figure 3 shows the TPR profile for a typical run. In comparison with the CuO results, the TPR profile of the NiO/SiO$_2$ material is fairly

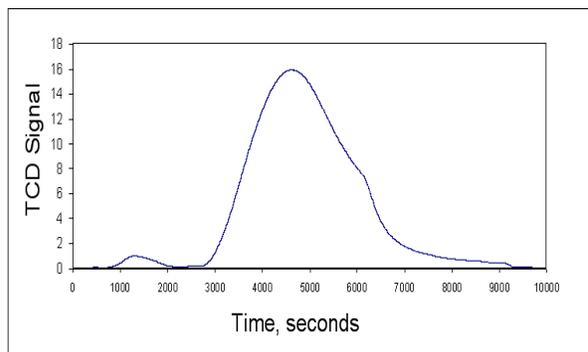symmetric and appears totally reduced by about 400ºC.

Figure 3. TPR profile of 69% NiO/SiO$_2$.

As in the case for the copper oxide, the reduction traces were integrated and the percent reduction calculated based on the loop volume determined by direct injection (509 µL). Based on this, the loop volume is recalculated for 100% reduction. These results are shown in Table 3.

TABLE 3

Calculated percent reduction and loop volume using 69% Ni/SiO$_2$ as external standard

Sample weight, g	% Reduction, calculated using 509 µL loop	Recalculated Loop Volume, µL
0.0420	98.1	499.3
0.0931	98.5	501.3
0.1033	100.9	513.6
0.1065	102.0	519.2
	ave = 99.9 ± 1.9	ave = 508.3 ± 9.6

The results obtained using the NiO/SiO$_2$ material are in excellent agreement with the

manual injections. Even the standard deviations of the replicate measurements were similar, ca. 2%. The advantage of this technique is that it makes it unattended and, perhaps more importantly, operator-independent. Other catalysts may be used, as long as their reducibility is known. Excellent results have been obtained with a "home-made" 10% Ni/SiO_2, which reduces 100%.

TEMPERATURE CALIBRATION AND DEAD VOLUME

Calibrating the temperature is somewhat more difficult as the temperature corresponding to a particular TCD signal depends on a number of factors, such as exact thermocouple placement, temperature ramp rate, gas flow rate, sample tube size, and catalyst bed volume. These items are all related to the dead volume or dead time of the particular experiment.

Nevertheless, it is important to know the accuracy of a temperature measurement. One option is to obtain a "certified" or "calibrated" thermocouple and trust its readings, realizing that after a few ramps the calibration may no longer be valid.

Another option is to check the approximate accuracy of the measurement thermocouple by measuring the decomposition of a well-studied material and comparing the observed temperature maximum with literature values.

Calcium oxalate monohydrate has been studied extensively in thermal analysis (3, 4) and is commonly used as a calibration material in TGA instrumentation. The decomposition of the oxalate occurs in three distinct steps, viz:

Steps for Calcium Oxalate Decomposition

(1) $CaC_2O_4 \cdot H_2O \rightarrow CaC_2O_4 + H_2O$
$$T_1 \leq 200°C$$

(2) $CaC_2O_4 \rightarrow CaCO_3 + CO$
$$T_2 \approx 500°C$$

(3) $CaCO_3 \rightarrow CaO + CO_2$
$$T_3 \approx 720°C$$

One can examine the decomposition of calcium oxalate using a TPR procedure in the AMI-200 instrument. Figure 4 shows the results using approximately 0.1 g of the oxalate and 25 sccm of helium as a carrier gas. The thermocouple was placed in direct contact with the bed of the material. The water peak is generally broad in these experiments. The temperature maxima obtained in these runs are in excellent agreement with the literature indicating accurate temperature measurement in the AMI-200.

For these measurements all extraneous sources of volume were minimized: the sample tube used was a straight 1/4" U-tube and the conventional water trap was replaced with a 1/16" short length of tubing.

The dead time between the sample and the detector can be minimized by using higher flow rates. In order to estimate the dead time, and hence the dead volume, several runs were performed at different carrier flow rate. Table 4 shows some typical results of these measurements.
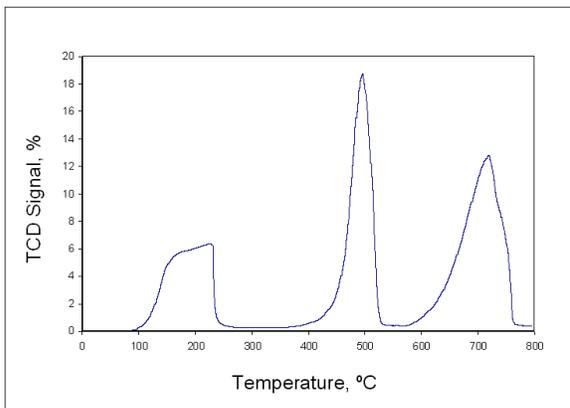
Figure 4. Decomposition of calcium oxalate monohydrate using an AMI-200 instrument. Conditions as follows: sample size ≈ 0.1 g; starting temperature = 25ºC; final temperature = 800ºC; ramp rate = 10ºC/minute; carrier flow rate = 25 sccm helium.

Looking at the sharpest of the three peaks, i.e, the second peak (corresponding to T_2), one sees minimal changes in the maxima as the flow rate is varied from 25 to 100 sccm, i.e., all three measurements are within experimental error. This indicates a very small dead volume past the sample bed. In fact, we estimate the dead volume between the sample and the TCD detector to be less than 2 mL. Naturally, if a larger diameter sample tube and a water trap were used the dead volume would be larger.

TABLE 4

Effect of carrier flow rate on peak maxima from calcium oxalate monohydrate

Carrier gas flow rate, sccm	T_1 ºC	T_2 ºC	T_3 ºC
25	159-230	497	720
50	161-196	505	715
100	134	499	714

SUMMARY

This Altamira Note detailed some simple calibration procedures which should be routinely performed to ensure that your AMI instrument is performing satisfactorily and that your results are accurate.

REFERENCES

(1)   A. Jones and A. D. McNicol, Temperature Programmed Reduction for Solid Materials Characterization, Marcel Dekker, Inc. (1986).

(2) A 1.00 g of the reduced catalyst would contain 0.64 g of Ni (atomic weight = 58.69) and 0.36 g of SiO_2. After calcination, the Ni would be converted to NiO (molecular weight = 74.69) so that the NiO would now weigh 0.815 g. Thus the NiO percentage would be equal to $(0.815)/(0.815 + 0.36)$ x $100 = 69\%$.

(3) J. Paulik and F. Paulik, Comprehensive Analytical Chemistry, v.12, Elsevier (1981).

(4)   See, for example: www. anasys.co.uk/library/tga1.htm.