June 2012

Environmental Technology Verification Report

PICOMETRIX, LLC
T-RAY 4000® TIME-DOMAIN TERAHERTZ SYSTEM

Prepared by
Battelle

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The Business of Innovation

Under a cooperative agreement with

EPA U.S. Environmental Protection Agency

ETV ETV ETV

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Environmental Technology Verification Report

ETV Advanced Monitoring Systems Center

PICOMETRIX, LLC
T-RAY 4000® TIME-DOMAIN TERAHERTZ SYSTEM

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Notice

Foreword

The EPA is charged by Congress with protecting the nation's air, water, and land resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. To meet this mandate, the EPA's Office of Research and Development provides data and science support that can be used to solve environmental problems and to build the scientific knowledge base needed to manage our ecological resources wisely, to understand how pollutants affect our health, and to prevent or reduce environmental risks.

The Environmental Technology Verification (ETV) Program has been established by the EPA to verify the performance characteristics of innovative environmental technology across all media and to report this objective information to permitters, buyers, and users of the technology, thus substantially accelerating the entrance of new environmental technologies into the marketplace. Verification organizations oversee and report verification activities based on testing and quality assurance protocols developed with input from major stakeholders and customer groups associated with the technology area. ETV consists of six environmental technology centers. Information about each of these centers can be found on the Internet at http://www.epa.gov/etv/.

Effective verifications of monitoring technologies are needed to assess environmental quality and to supply cost and performance data to select the most appropriate technology for that assessment. Under a cooperative agreement, Battelle has received EPA funding to plan, coordinate, and conduct such verification tests for "Advanced Monitoring Systems for Air, Water, and Soil" and report the results to the community at large. Information concerning this specific environmental technology area can be found on the Internet at http://www.epa.gov/etv/centers/center1.html.

Acknowledgments

The authors wish to acknowledge the support of all those who helped plan and conduct the verification test, analyze the data, and prepare this report. We greatly appreciate the involvement and support of Appleton, for allowing testing to be conducted in their plant. We thank, in particular, the efforts of Mike Friese, Jason Morgan, and Dan Scholz of Appleton. We also thank the EPA Office of Air and Radiation for their support of this verification test. Finally, we would like to thank Paul Thomas, 3M; Mike Barlament, Kimberly-Clark; Temeka Taplin, Mele Associates; and Madeline Nawar, U.S. EPA Office of Air and Radiation for their review of this verification report. Quality assurance (QA) oversight was provided by Michelle Henderson and Laurel Staley, U.S. EPA, and Rosanna Buhl, Battelle.

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List of Abbreviations

ADQ	Audit of Data Quality
AMS	Advanced Monitoring Systems
DQI	data quality indicator
EM	electromagnetic
EPA	U.S. Environmental Protection Agency
ERS	External Reference Structure
ETV	Environmental Technology Verification
gsm	grams per square meter
LRB	laboratory record book (the test logbook)
PE	performance evaluation
ps	picosecond = 10^{-12} second
QA	quality assurance
QAPP	quality assurance project plan
QC	quality control
QMP	quality management plan
RI	Refractive Index
SOP	Standard Operating Procedure
TAPPI	Technical Association of the Pulp and Paper Industry
TD-THz	Time-Domain Terahertz
THz	terahertz
ToF	Time-of-Flight
TSA	Technical Systems Audit
μW	microwatt = 10^{-6} watt
VTC	Verification Test Coordinator

Chapter 1
Background

The U.S. Environmental Protection Agency (EPA) supports the Environmental Technology Verification (ETV) Program to facilitate the deployment of innovative environmental technologies through performance verification and dissemination of information. The goal of the ETV Program is to further environmental protection by accelerating the acceptance and use of improved and cost-effective technologies. ETV seeks to achieve this goal by providing high-quality, peer-reviewed data on technology performance to those involved in the design, distribution, financing, permitting, purchase, and use of environmental technologies.

ETV works in partnership with recognized non-profit testing organizations (such as Battelle); with stakeholder groups consisting of buyers, vendor organizations, and permitters; and with the full participation of individual technology developers. The program evaluates the performance of innovative technologies by developing test plans that are responsive to the needs of stakeholders, conducting field or laboratory tests (as appropriate), collecting and analyzing data, and preparing peer-reviewed reports. All evaluations are conducted in accordance with rigorous quality assurance (QA) protocols to ensure that data of known and adequate quality are generated and that the results are defensible.

The EPA's National Risk Management Research Laboratory (NRMRL) and its verification organization partner, Battelle, operate the Advanced Monitoring Systems (AMS) Center under ETV. The AMS Center recently evaluated the performance of the Picometrix, LLC, T-Ray 4000® Time-Domain Terahertz (TD-THz) System as an alternative to using sealed radioactive source nuclear gauges in industrial applications such as paper manufacturing. This test was conducted in conjunction with EPA's Alternative Technology Initiative, which aims to encourage voluntary replacement of sealed nuclear devices with non-nuclear sources.

Chapter 2
Technology Description

This report provides results for the verification testing of the Picometrix, LLC, T-Ray 4000® TD-THz System. The following is a description of the system, based on information provided by the vendor. The information provided below was not verified in this test.

TD-THz systems (shown in Figure 2-3) emit and detect a very narrow (<1 picosecond [ps]) electromagnetic (EM) pulse that forms photons in the THz frequency range. The THz frequency range falls between microwaves (0.1 THz) and far infrared (IR) (10 THz). TD-THz systems measure the electrical field strength of the EM photon pulse as a function of time. Most dielectric materials are transparent in the region of study with TD-THz (0.05–3 THz). Plastics (regardless of color), paper, textiles, dry wood, packaging materials, rubbers, foams, non-polar liquids (such as oils), paints (including low observable "radar absorbing") and other coatings are all transparent to THz wavelength photons. Polar liquids (such as water and alcohols) are strongly absorbing over the THz frequency region. The EM photon pulse is also non-ionizing and thus safer than sealed radioactive source techniques.

The THz pulse is low energy (less than 1 microwatt [μW]) and can be focused, reflected, and treated essentially in the same manner as any pulsed photon (light) source. After this photon pulse has interacted with matter (transmission, reflection, and scatter), the changes in the pulse lead to two primary methods of analysis, spectroscopic and Time-of-Flight (ToF). Spectroscopic methods of investigation are possible with THz. The transformation of the TD-THz data using a Fourier function to better understand the time and frequency domains of the data allows time and spectroscopic analysis. The second common method of analysis is to directly study the TD data by measuring changes in the ToF of the photon pulse as it interacts with matter.

Analysis of ToF for the THz pulses can be used to determine the basis weight (mass per unit area) of manufactured products. A material's ToF value is found in the following manner: when photons transmit through a material, the transit time of the photon will be increased due to the increased refractive index (RI) of the material compared with the RI of photons in air or vacuum (~1). The ratio of the velocity of photons in a vacuum to the velocity of photons in the material of interest defines the RI for that material. Because the velocity of the EM is less in a material, the amount of time required for the EM to transmit through the material will be longer. The difference in time between the EM pulses transmitting through the material, compared with the same transmission through air, although extremely small can be precisely measured with THz instrumentation. This difference is the ToF delay. This ToF delay (typically in ps) is calibrated against basis weight values for the sample material determined using laboratory measurements. The THz method to measure a material's basis weight is to measure the RI that causes the increase of the ToF of the EM pulse as it transmits through the material of interest. This ToF value, which can be translated to an RI, is calibrated against accepted values of the material's RI and basis weight. The THz method is a time-based measurement, as opposed to the amplitude attenuation-based measurement method of nuclear gauges.

The measurement of basis weight is the most common use for nuclear gauges in industry. The Appleton Paper Company, Appleton WI (Appleton), routinely uses nuclear gauge technology and Technical Association of the Pulp and Paper Industry (TAPPI) laboratory measurements for its business and maintains an appropriate safety license to operate a nuclear gauge. The recognized TAPPI procedure for basis weight is to measure the basis weight of a specific area of a sheet product (e.g., paper) under controlled laboratory conditions using an analytical balance. The specific area cut from the sheet product varies depending on the product. Example basis weight units of measure are pounds per square yard or grams per square meter. For the paper industry, a common unit is pounds per ream, where a ream represents 3,300 square feet of paper.

A wide range of material basis weight values (5 grams per square meter [gsm] to greater than 100,000 gsm) can be measured with this single source THz instrument. The THz system directly measures the ToF increase due to the pulse passing through the material under test. Formally this increase in ToF is the volume of material in the beam path times the RI of the material at the THz frequency minus 1. Finally, the amplitude of the transmitted THz pulse may be configured to provide simultaneous complementary information related to the chemical and physical properties of the sample, including moisture content. In this verification test, a distinction was made between a measurement of thickness (sometimes called caliper thickness) or the physical dimension of the material under test, and the basis weight, which is the mass per unit area. A nuclear gauge measures the amount of matter between the source and detector, which is most directly converted to basis weight. In circumstances where the material has a uniform density, the nuclear gauge measurement can also be correlated to physical thickness.

Most THz measurements are made in reflection, as this geometry simplifies the system configuration and reduces cost. Often, a fixed metal plate is installed behind the sample. The THz pulse, reflected off a rear metal plate, will have transmitted through the sample twice. This measurement mode is equivalent to double pass transmission and the measured ToF delay is therefore increased by a factor of two.

The use of a beam splitter in the reflection sensor allows the transmitting and reflecting THz pulses to remain collinear throughout the inspection (see Figure 2-1). Therefore, the sensor operates best when aligned orthogonal to the inspection surface. However, for illustration purposes, an angle is often shown between the transmitter and receiver (see Figure 2-2). This display method helps to clearly separate the incoming and reflecting THz pulses and thus better illustrates the origin and timing of the reflection pulses.

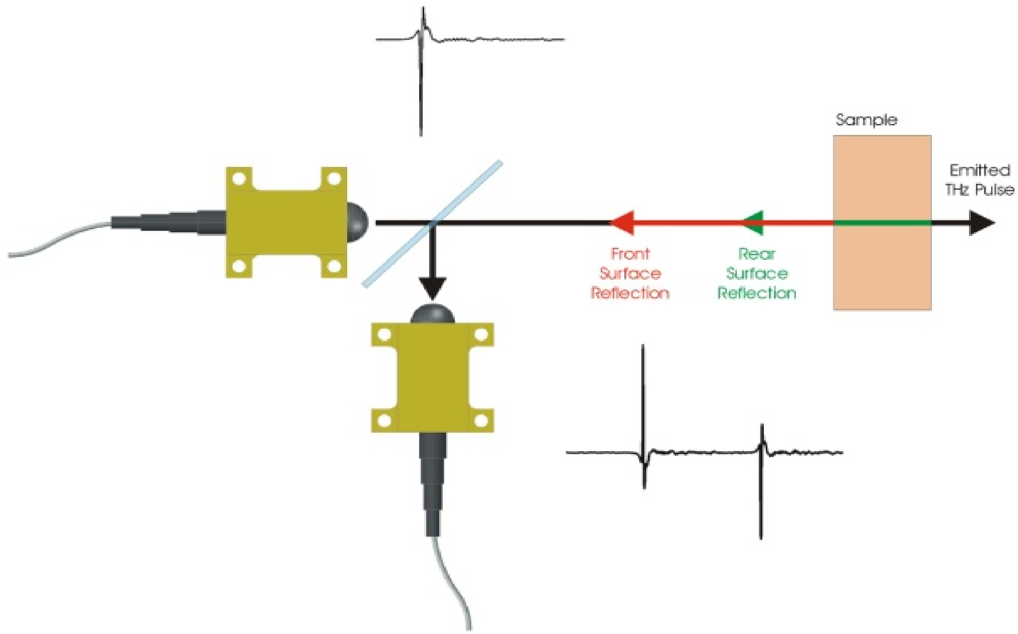

Figure 2-1. Collinear THz Reflection Sensor (with Beam-Splitter)

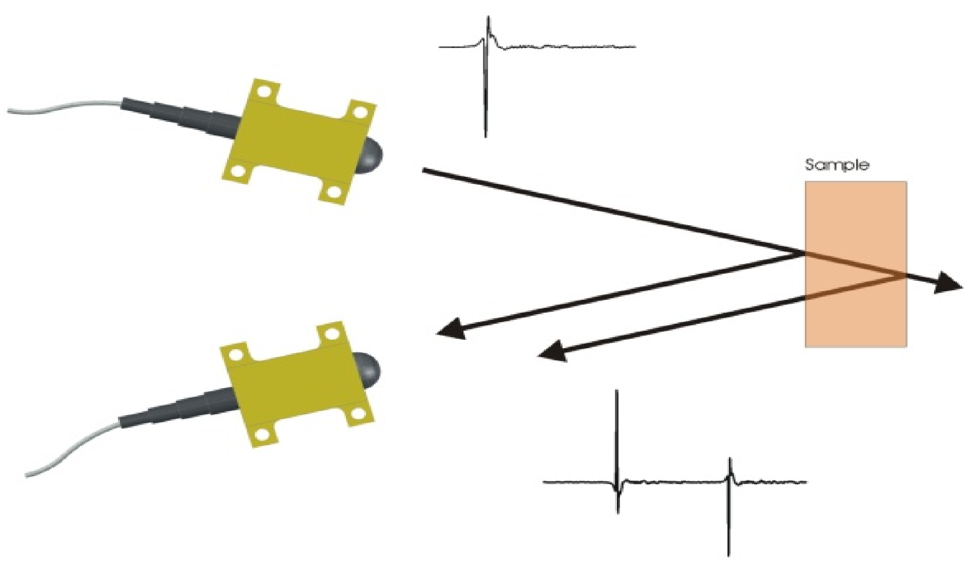

Figure 2-2. Illustration of Photon Pulse's Origin and Detections

Because the most common use of nuclear gauges in industrial settings is the measurement of basis weight, this verification test compared basis weight values determined by these two systems vs. the laboratory-generated basis weights measurements.

The fundamental method of nuclear gauges to find basis weight is to calibrate the measured attenuation of the nuclear particle flux when passing through a sample against a standard-method-determined or accepted basis weight value. If the average density of the product is known and remains constant, then the average sample thickness can be calculated from the measured basis weight value.

The fundamental measurement with a THz sensor is the delay in the ToF of the THz pulse as it passes through a sample. In a transmission measurement, the delay can be directly measured and then calibrated against basis weight, a similar process to nuclear gauges. The sample's ToF is calibrated against a standard method determined or accepted basis weight values.

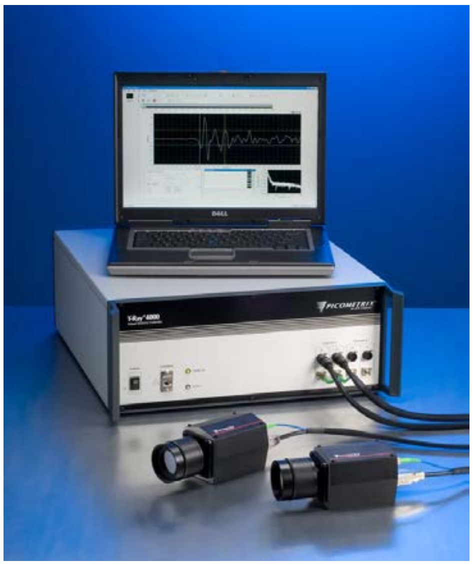

Figure 2-3. Picometrix, LLC, T-Ray 4000® Time-Domain THz System

Chapter 3
Test Design and Procedures

3.1 Introduction

This verification test was conducted according to the technical and quality assurance/quality control (QA/QC) procedures specified in the *Quality Assurance Project Plan (QAPP) for Verification of Picometrix, LLC, T-Ray 4000® Time-Domain Terahertz System*(1) and complied with the data quality requirements in the AMS Center Quality Management Plan (QMP).(2) As indicated in the QAPP, the testing conducted satisfied EPA QA Category II requirements, which establishes QAPP requirements for important, highly visible Agency projects involving areas such as supporting the development of environmental regulations or standards.. The QAPP and this verification report were reviewed by:

- Paul Thomas, 3M
- Mike Barlament, Kimberly-Clark
- Temeka Taplin, Mele Associates
- Madeleine Nawar, U.S. EPA.

Battelle conducted this verification test with funding support from the EPA's Office of Air and Radiation.

3.2 Test Design

A non-radio isotopic source THz technology (Picometrix, T-Ray 4000® Time-Domain Terahertz System) was tested at Appleton Paper Company, in Appleton WI. This allowed for performance evaluation under real world manufacturing conditions. The performance of the THz technology was verified based on accuracy, precision, comparability, and operational factors. The test design consisted of a production line and a laboratory phase.

The performance of the technology was tested using two different weights of paper –mid-weight and heavy weight. For each paper type, five separate rolls (treated as lots by Appleton) were tested resulting in ten sets of synchronized nuclear gauge and THz sensor data collected during the actual production process (i.e., the production line phase). All steps within a single lot run were completed within a single roll of product. A paper sample was collected from the end of each roll used for production line testing. The 10 samples collected from these runs were used for testing during the laboratory phase. The paper sample basis weight from each lot was measured using standard TAPPI gravimetric protocols, cut into small squares, stacked, and the

ToF measured for each stack using the THz technology on a stable mount. A qualified Appleton technician conducted all reference measurements for this verification test according to procedures described in Appleton Standard Test Method 10001.00 *Basis Weight – Laboratory Determination of Coated and Uncoated Paper*[3] as modified in the QAPP.

The nuclear gauge technology was a Measurex, MX Open system, and was owned by Appleton and operated by qualified Appleton staff according to standard Appleton procedures. The Picometrix THz technology was operated by the vendor for both the production line and laboratory phases. Testing was conducted over three days. Production line and laboratory measurements for medium-weight paper took place on February 16 and 17, 2011. Testing on the heavy-weight paper took place on February 23, 2011.

3.2.1 Production Line Testing

Production line testing involved measuring paper basis weight simultaneously using the nuclear gauge and a THz sensor installed in the line. For testing purposes, the THz sensor was bolted to a mounting bracket at a fixed position approximately 2-5 inches from the edge of the moving paper sheet. The production nuclear gauge system was mounted on a scanner frame which normally moves back-and-forth across the sheet. For verification testing, the nuclear gauge system was "parked" at the edge of the paper and the THz sensor aligned with the nuclear gauge between 2-5 inches from the edge of the sheet. Both the THz sensor and nuclear gauge remained stationary during testing. Figure 3-1 shows a schematic of the gauge positions and Figure 3-2 shows the nuclear gauge and THz sensor during production line testing. Figure 3-3 shows a close-up of the THz sensor during testing.

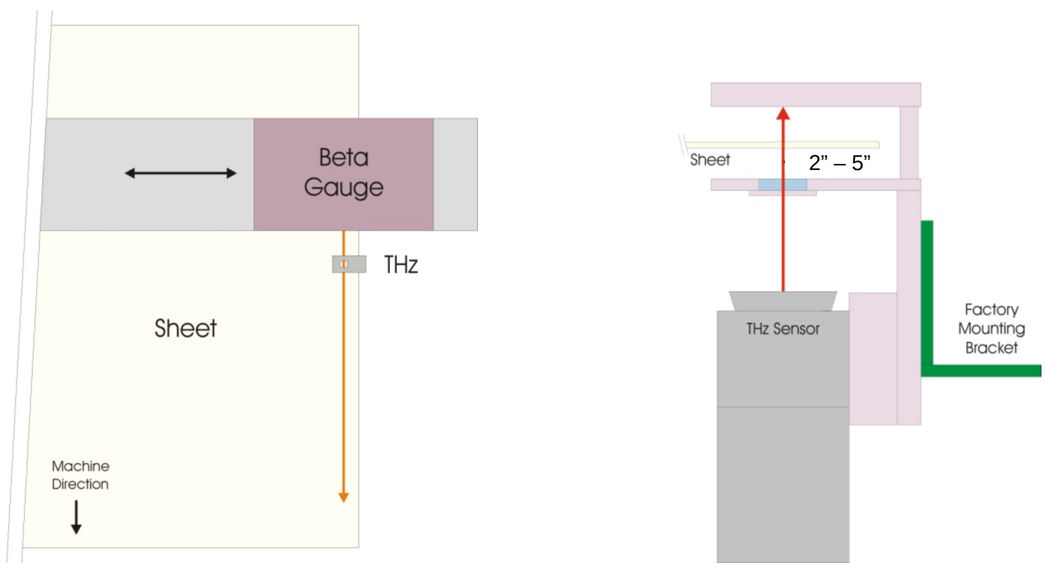

Figure 3-1. Relative Position of Sample Paper Sheet, Nuclear (Beta) Gauge, and THz Sensor

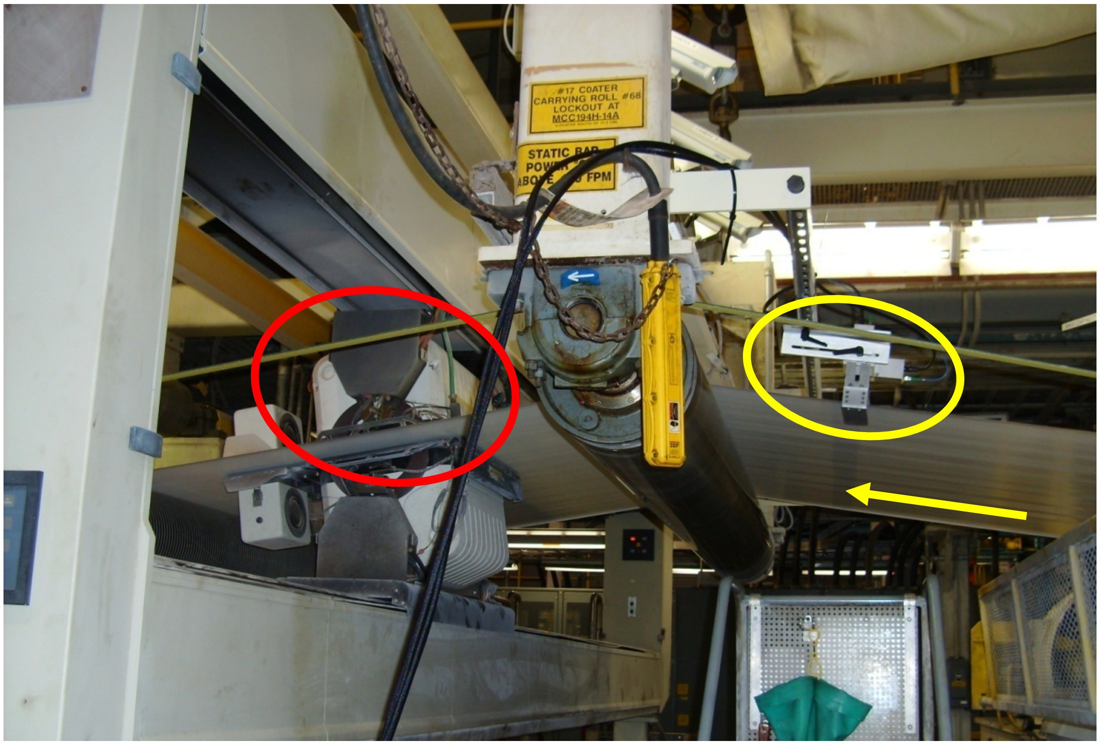

Figure 3-2. THz Sensor and Nuclear Gauge During Production Line Testing. The THz sensor is seen to the right on a mounting bracket (Yellow oval). The nuclear gauge housing is seen to the left of the roller (red oval). The arrow denotes paper flow.

Figure 3-3. Close-up of THz Sensor in the Production Line. The paper on the production line is seen between the two lower plates of the gauge. The yellow arrow indicates the THz photon path.

Ten lots of paper were tested in a standard paper coating production line; five mid-weight and five heavy weight paper products. The process was identical for each lot. Production of either the mid-weight or heavy-weight was initiated; production parameters were monitored via Appleton's computer-based data collection system. During the monitoring period, the nuclear gauge was sweeping back and forth across the moving paper sheet collecting continuous measurements. This process took from three to six hours, depending on the number of coatings being applied and production issues during any of the runs. As part of their standard manufacturing procedure, each production run was assigned a Reference Roll Number. This number was logged in the trial notebooks and used to track individual samples.

Once proper manufacturing stability was confirmed by the Appleton production representatives, the nuclear gauge was moved to the edge of the paper and parked as close to the edge as possible; the THz sensor was then aligned as precisely as possible, using manual inspection with a 1/16 inch scale ruler, to the same location on the sheet (cross direction) as that of the nuclear gauge. A difference between the THz and nuclear scan spot of ¼ inch was possible. The nuclear scan spot was typically 2 inch in diameter, and the THz sensor spot was ¼ of an inch, so an offset of the ¼ inch from the center of the nuclear gauge scan spot was not thought to be significant. During the 10 runs, the sensor positions (together) ranged between 2 and 5 inches from the edge of the sheet. The sheet edge position varied from product to product, hence the variation in the distance from sheet edge. The THz sensor was positioned as close as possible along the direction of material manufacture (machine direction), within five feet in front (downstream) of the nuclear gauge.

Immediately before sample data collection for each lot, the THz sensor assembly was rotated "off-sheet", i.e., so that there was no paper in the measurement path. In this off-sheet position, a system check was conducted that made ToF measurements of the air space between the upper and lower plates of the sensor assembly. These 'open-air space' data were collected for approximately two seconds and stored for use in the basis weight calculation. The sensor was then rotated back to the fixed position aligned with the nuclear gauge. On-line data collection began within one minute after the completion of this procedure, and was simultaneously collected and logged for both the nuclear and THz systems for a continuous period of at least five minutes. The nuclear gauge was moved off-sheet and parked 16 seconds before the end of the roll[1] and an end-of-run two-second ToF open air space THz system check was performed (Figure 3-4). At the end of each lot roll, an end-of-roll "tear-off" paper sample was collected. These samples were marked and saved for laboratory and THz inspection. To ensure data comparability, the time of each of these events was documented in the data log.

[1] The nuclear gauge moved off-sheet (i.e., ending on-line measurements) 16 seconds before the end of a roll. This step was required to allow an individual to paste the end of the previous paper roll to the beginning of the next roll. Once the start of the new production roll was past the inspection point, the nuclear gauge returned to scanning the product.

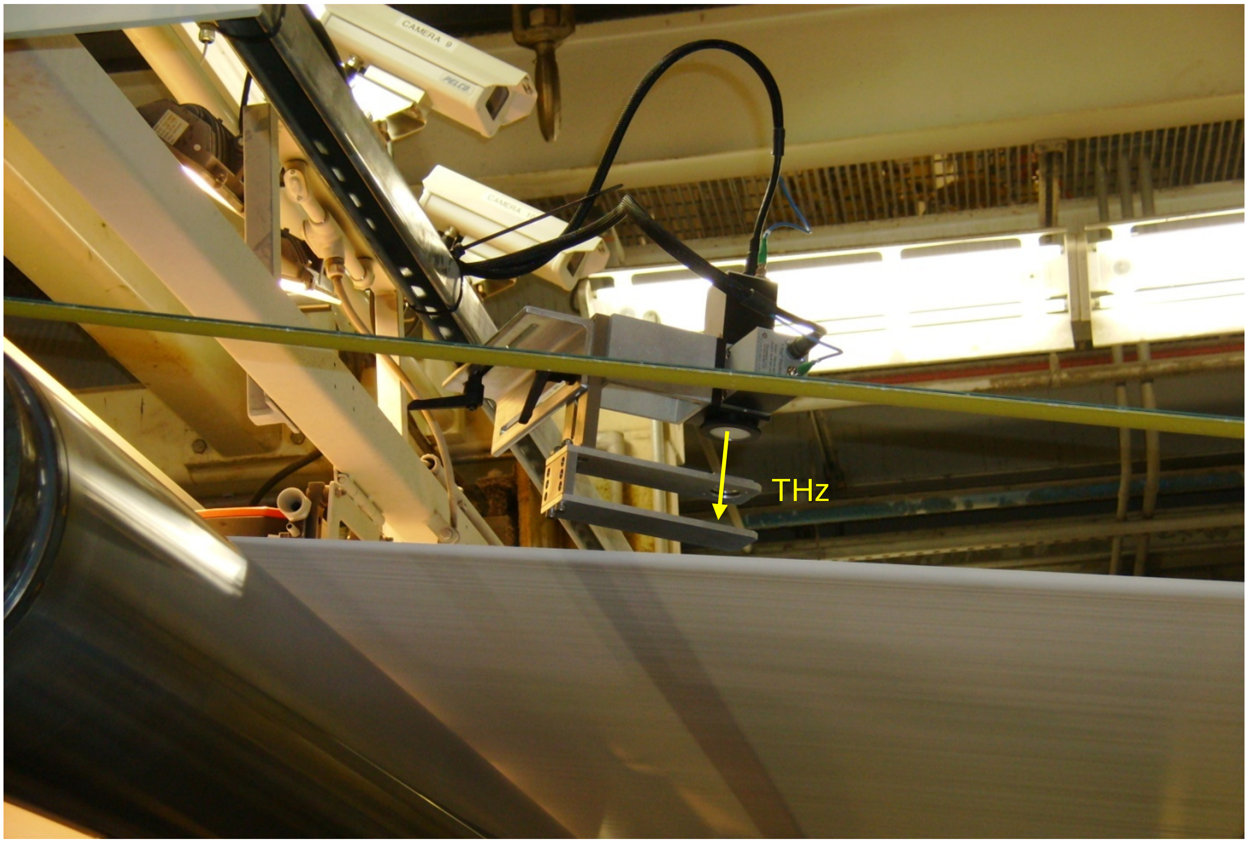

Figure 3-4. THz sensor rotated 'off-sheet' for air space reading

The data collected throughout each run was time stamped by each technology; nuclear gauge to 5 second increments and THz results to 0.01 second increments. This time stamp data allowed the two technology results to be more precisely aligned. Within 10 minutes after each data collection run, the two technology system clocks, used to timestamp the nuclear gauge and THz data were compared and recorded to within a ±1 second increment for both technologies.

The nuclear gauge acquired measurements at a 1/5 Hz rate. Thus, a 5-minute period would result in a log of 60 nuclear gauge measurements. The THz system acquired measurements at a 100 Hz rate, thus 30,000 measurements were collected over the 5-minute period. At the mid-point of each day of testing, the THz system time measurement calibration was checked (System Check). This calibration procedure followed protocols established by Picometrix.

The nuclear gauge was operated and calibrated according to manufacturer recommendations and established Appleton protocols.

Environmental conditions during the production line testing were not controlled for ETV testing purposes. Thus, both gauges operated in a manufacturing factory environment within the Appleton production facility. Environmental conditions during testing are presented in Table 3-1 based on independent observations made by a Battelle staff member who was present throughout testing and who conducted independent monitoring of temperature and relative humidity on the production floor and in the laboratory. A hand-held Hobo/Onset Model H14-002 monitor was used to monitor production floor temperature and relative humidity. The instrument was calibrated in Battelle's ISO 17025 calibration laboratory prior to testing. Data were recorded via a data logger.

3.2.2 Laboratory Testing

The purpose of laboratory testing was to provide a direct comparison between THz ToF basis weights and the basis weights determined using standard TAPPI gravimetric analysis made on the "tear-off" samples collected at that end of each roll of paper used for production line testing. Five tear-off samples were collected for each paper weight (i.e., one from each of five mid-weight rolls and one from each of five heavy-weight rolls tested). The same THz sensor that was used in production line testing was moved to the TAPPI room for static off-line THz measurements. Laboratory testing was performed in a TAPPI room located on the manufacturing floor. The environment of this room was tightly controlled (72 °F and 50% RH). Laboratory basis weights were measured by trained Appleton laboratory personnel. Each "tear-off" paper sample was folded into four layers and cut precisely into 9.5 x 12.5 inch squares, creating a 475 square-inch sample. The sample was weighed on an analytical Mettler balance calibrated to read basis weight (lb/ream) directly for this sample size. The laboratory-measured basis weights were recorded by a Battelle staff member into the project logbook. The ongoing and overall basis weight for each paper lot (roll) was also determined on the production line by the nuclear gauge and the Appleton production process control software. Figures 3-5 through 3-7 show pictures from the laboratory testing phase.

Once basis weight determination was complete, the mid-weight paper was cut into 96, 2-inch squares. Further details on the cutting size are provided in Section 6.2. Eight stacks of 12 squares were then created. Each stack was placed in the THz sample holder and measured for approximately 30 seconds, or until the ToF value was stable. The same process was used for both paper weights except that for the heavy-weight paper the 2-inch squares were measured in 16 stacks of six pieces each because the extreme thickness of the paper resulted in a noisy signal. Thus eight replicate measurements for the mid-weight paper and 16 replicate measurements for the heavy-weight paper were collected by the THz technology. These results were used in the precision calculations. The precision results of these measurements are discussed in Chapter 6.

For one mid-weight sample, three replicate samples were cut for basis weight measurement to assess cutting variability. For one heavy-weight 6-piece stack, three separate THz measurements were collected to assess measurement reproducibility.

The QAPP specified that the laboratory results from the first data collection run would be used to temporarily calibrate the THz sensor to output basis weight values. This proved impractical due to the production schedule and availability of Appleton staff to perform the basis weight measurements. Therefore, a deviation was prepared, and all "raw" THz measurement values were saved and post-calibrated once all measurement results were available.

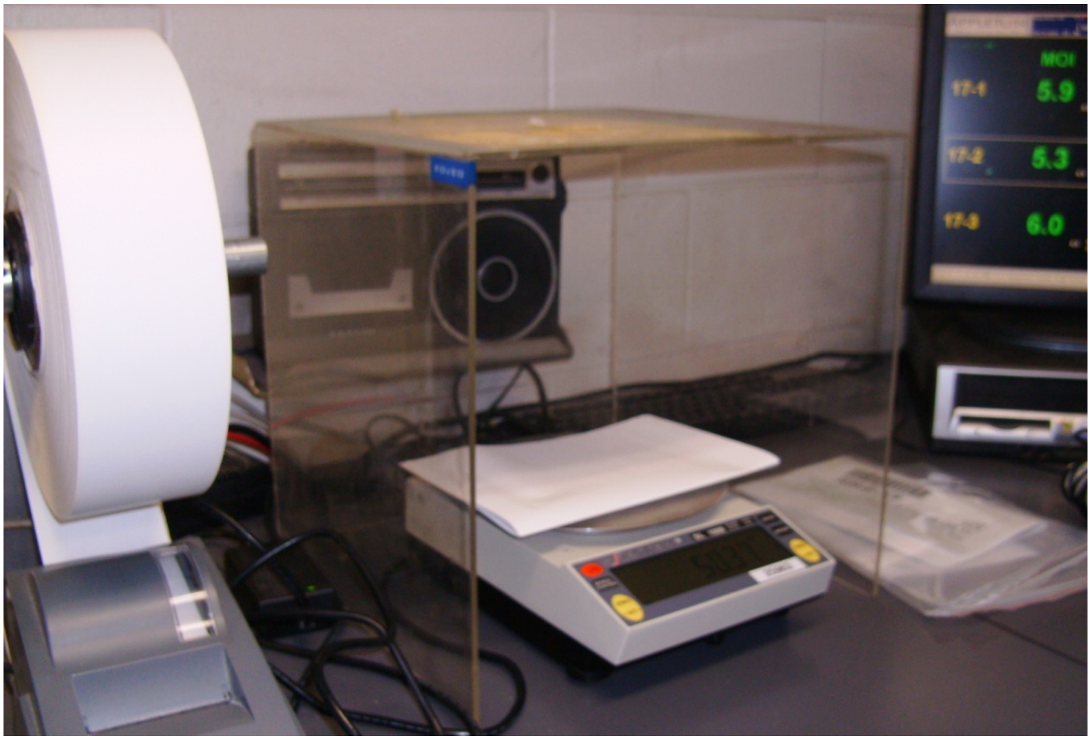

Figure 3-5. Standard Basis Weight Determination using an Analytical Balance. The balance is calibrated to read basis weight when four 9.5 inch x 12.5 inch sheets are weighed.

Figure 3-6. THz sensor system in the Laboratory. One stack of mid-weight paper is seen in the sample holder (highlighted in a yellow oval).

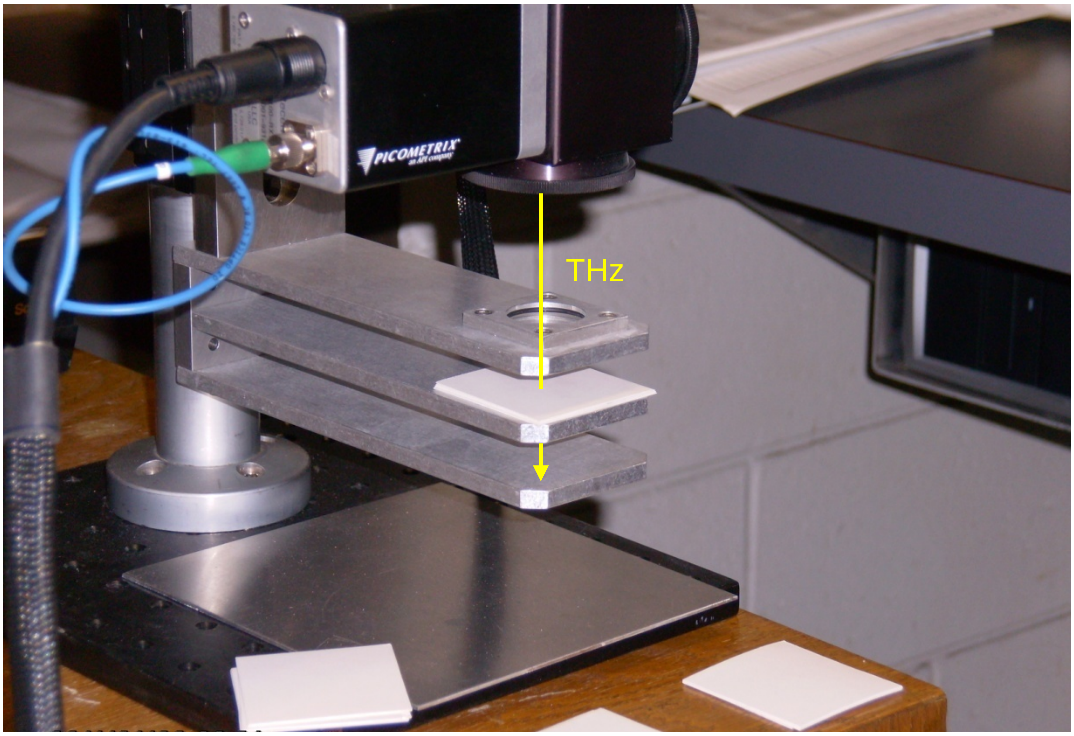

Figure 3-7. Close-up of THz sensor system in the Laboratory

3.3 Test Samples

Laboratory samples were collected at the end of each roll for which a set of nuclear and THz sensor measurements were collected. Thus, five laboratory samples were collected from both the mid-weight and heavy-weight paper stocks. Approximately 50 feet of paper were removed and discarded from the end of each roll to eliminate any end-of-roll artifacts. Then approximately 6 feet from the 12 foot wide roll were collected, folded, labeled and transferred to the production-floor laboratory within the Appleton production facility. The samples were then conditioned for at least 10 hours in the room where they would be evaluated before laboratory analysis.

3.4 Test Conditions

Temperature and relative humidity can impact basis weight values. Therefore, TAPPI standard T402 sp-03 *Standard Conditioning and Testing atmospheres for paper, board, pulp handsheets, and related products (2003)* specifies the environmental conditions under which basis weight should be determined:

Temperature: 23±1.0 °C (73±1.8 °F)
Relative Humidity: 50%±2.0%

A hand-held Hobo/Onset Model H14-002 monitor was used by Battelle to measure temperature and relative humidity throughout testing. These values were monitored on both the production floor and the room used for laboratory analysis. The Hobo monitor gathered and stored data at 30-second intervals. The files were downloaded for analysis at the end of each test day. Table 3-1 summarizes the actual environmental conditions measured by Battelle during testing. Shaded values indicate environmental condition in excess of the TAPPI standards.

Table 3-1. Environmental Conditions During Testing.

Sample ID	Production Line			Laboratory		
	Sample Run Time	Temperature (°F)	Relative Humidity (%)	Sample Run Time	Temperature (°F)	Relative Humidity (%)
	Mid-weight Feb 16, 2011			Mid-weight Feb 17, 2011		
ACA11B16026	15:32	77.3	24	09:56	75.2	46
ACA11B16027	15:55	78.0	23	10:16	75.2	47
ACA11B16028	16:16	76.6	25	10:36	75.2	46
ACA11B16033	17:20[1]	n/a-[2]	n/a-[2]	09:14	71.8	41
ACA11B16035	18:20	n/a-[2]	n/a-[2]	11:06	75.2	46
ACA11B16037	19:29	71.8	53	11:20	75.2	46
	Heavy-weight Feb 23, 2011					
ACA11B23035	11:54	75.9	17	20:44	72.5	50
ACA11B23036	12:14	76.6	18	18:33	72.5	52
ACA11B23042	14:12	75.9	17	19:52	72.5	50
ACA11B23043	14:32	74.5	19	20:10	72.5	49
ACA11B23044	14:48	75.2	19	20:30	72.5	50

[1] Only laboratory data were collected for this lot; the THz system collected data to the wrong channel thus there is no associated THz data.
[2] The Hobo unit was moved to the Laboratory to monitor the TAPPI room conditioning environment during collection of these samples.

For most production line testing and mid-weight paper laboratory testing, temperature exceeded the TAPPI standard for basis weight measurement and relative humidity was lower than the standard. It should be noted that the temperature and relative humidity of paper in the production line was controlled through the process and that air temperature is not a reliable surrogate for paper conditions. During laboratory testing on February 17, 2011, conditions did not meet TAPPI standards. This was due to the frequent opening of the laboratory door by Appleton staff that monitored production problems. While this room's environment may have had an impact on the testing results, observations during measurements indicate that prolonged handling of the paper stacks had a much larger effect. For some paper stack samples, a much longer data collection time was used to allow the THz reading to stop decreasing and stabilize. It has been assumed that this was due to moisture in the paper stacks, gained during handling, being lost while equilibrating in the room environment. Thus, the minor room environmental condition inconsistencies were thought to be inconsequential. The increased time for data collection (up to 30 seconds) for some laboratory paper stack measurements was also considered inconsequential.

3.5 Testing Parameters

Test parameters for this validation test included: accuracy, precision, comparability, and operational factors. The results for each parameter are discussed below.

3.5.1 *Accuracy*

Accuracy was assessed by evaluating the basis weight determined by the Picometrix, LLC, T-Ray 4000® TD-THz System against basis weight measured using the standard laboratory method. For the production line samples, the comparison of accuracy was limited because the THz system ToF measurements made during production line runs were not made on the exact same location on the paper as the laboratory samples collected from the end of the roll. To address this complication, off-line static THz measurements were made on the paper samples in the laboratory. By making a large number of measurements over the spatial area of the lab sample, the accuracy of the THz measurement could be assessed. Thus, only offline THz measurements and laboratory basis weight results were used to assess the accuracy of the Picometrix THz technology. The results are summarized in Chapter 6.

3.5.2 *Precision*

The precision of the Picometrix, LLC, T-Ray 4000® TD-THz System was assessed by triplicate THz measurements of one stack of the heavy paper used for laboratory basis weight determination. The stack contained six, 2 inch square samples. In addition, the cutting precision of the 9.5 inch x 12.5 inch paper sample was assessed by cutting and weighing three mid-weight samples from Sample ACA11B16028. The results are summarized in Chapter 6.

3.5.3 *Comparability*

This test assessed the performance of the Picometrix, LLC, T-Ray 4000® TD-THz System based on the measurement of whole sample basis weight as compared to laboratory basis weight values. A second comparison was also made between the THz sensor and nuclear gauge based on production line testing results. For this comparison, results from the nuclear gauge and THz sensor were directly evaluated against each other for comparability. Data obtained by each technology were assessed on a roll by roll basis for comparability. Because of the operational need to remain static for this testing, cross-sheet scanning was not conducted. An additional factor limiting comparison was the difference in measurement spot size between the two technologies. The results of the comparison are presented in Chapter 6.

3.5.4 *Operational Factors*

Operational factors such as maintenance needs, power needs, calibration frequency, data output, consumables used, ease of use, repair requirements, training and certification requirements, safety requirements and image throughput were evaluated based on Battelle staff testing observations and input provided from Picometrix staff. The results are summarized in Chapter 6.

Chapter 4
Quality Assurance/Quality Control

QA/QC procedures were performed in accordance with the QMP for the AMS Center[2] and the test/QA plan for this verification test.[1] QA/QC procedures and results are described below.

4.1 Quality Control

4.1.1 Instrument Calibration Checks

The THz system was set up at the beginning of each test day to optimize the signal. A standard fused silica block was used to establish the initial signal output. As part of the QA/QC requirements for the verification test, the system was checked mid-day (Section 4.2.2) to verify that the system was still operating correctly and that no drift had occurred.

The balance, temperature measuring device, and hygrometer were calibrated according to the manufacturer's specifications and Appleton procedures prior to testing. More details are provided in Table 4-1. The nuclear gauge, a Measurex, MX-Open system, was calibrated by the Appleton plant operator in accordance with the manufacturer's specifications and Appleton procedures.

4.1.2 Laboratory Replicate Samples

The largest variable in laboratory basis weight determination was the precision with which the sample was cut to an exact size for each basis weight measurement. To address this issue, three test samples were cut from one of the mid-weight samples and weighed using the TAPPI standard method to identify the error associated with the cutting precision. The average and standard deviation of three replicate samples was 48.85 ± 0.18 lb/ream and the coefficient of variation 0.36%. This variability was considered low and was within TAPPI standard limits. Thus, no adjustments were made to the laboratory data or considerations made for interpreting the data analysis results.

4.1.3 Data Quality Indicators

The QAPP defined data quality indicators (DQIs) that would enable stakeholders to assess whether the verification test provided suitable data for a robust evaluation of performance. DQIs were established for paper basis weight measurements and the laboratory analyses that required control for this performance-based measurement. The DQI for these supporting measurements are quantitatively defined in Table 4-1, along with the acceptance criteria and whether the criteria were achieved.

Table 4-1. DQI and Criteria for Critical Supporting Measurements

Phase	DQI/Critical Measurement	Method of Assessment	Frequency	Acceptance Criteria	Criteria Achieved?
Laboratory[1] Confirmation	Accuracy/Balance[2]	Certified weights	Quarterly by professional balance service and Prior to testing	NIST tolerances for analytical balances	Yes. Balance calibrated 1-31-2011
Laboratory Confirmation	Accuracy/TAPPI Room Temperature	Thermometer	Continuously during testing	23±1.0 °C (73±1.8 °F)	Yes. Powers monitor calibrated 12-7-2010
Laboratory Confirmation	Accuracy/TAPPI Room Relative Humidity	Hygrometer	Continuously during testing	50%±2.0%	Yes. Powers monitor calibrated 12-7-2010
Laboratory Confirmation	Hygrometer	ISO 17025 Certified Laboratory	Annually and within 1 week of testing	±1.0% at 23°C and 50% RH	Yes. Hobo calibrated 2-11-2011
Laboratory Confirmation	Thermometer	ISO 17025 Certified Laboratory	Annually and within 1 week of testing	Graduated to 0.20 °C (0.50 °F)	Yes. Hobo calibrated 2-11-2011
In-line Production	Completeness/ Amount of THz data collected per second	Time stamp of THz data stream	Each run: number of data points/ second	>99%	Yes 100%
In line Production	Accuracy/THz instrument calibration	Calibration standard results vs. initial calibration	Daily Mid-day check	$\pm 20^{-15}$ sec	No. Test devised for trial was not reliable
In line Production	Accuracy/Amount of accurate data collected	Review data for anomalies (> ±5% from average)	Each run	<20% of data average	Yes All > 80%
Off-sheet Production	Accuracy/mass in chamber	Off-sheet check of optics	Before and after each run	$< \pm 50^{-15}$ sec difference between readings	Yes All results $< \pm 5^{-15}$ sec

[1] Laboratory Confirmation was the reference method for this test.
[2] Basis weight determined using Appleton Spec. No. 10001.00 which was based on TAPPI T 410.

4.2 Equipment Testing, Inspection, and Maintenance

All laboratory equipment was tested, inspected, and maintained according to Appleton internal requirements and TAPPI standards to ensure that the performance requirements established in the QAPP(1) were achieved.

4.2.1 Hobo Continuous Reading Monitor

A hand-held Hobo continuous-recording monitor was used to verify the accuracy of the TAPPI room temperature and relative humidity equipment. A comparison of seven concurrent readings during testing verified that the temperature percent difference ranged from 0.14% - 4.21% and that the relative humidity percent difference ranged from -5.58 to 5.63%. Based on these percent difference values, the temperature and relative humidity from the TAPPI room and Battelle ISO 17025 certified monitors were considered comparable, and thus TAPPI room measurements were considered representative of the laboratory testing environment.

4.2.2 THz Operation Verification

THz Systems Checks. THz instrument system checks were performed on each production line test day and the laboratory static test day for the heavy-weight paper; however due to an oversight, the THz system check was not performed on the day that the mid-weight paper was tested in the laboratory. The QAPP specified that the checks should be $\pm 20^{-15}$ seconds vs. the initial set-up signal optimization. The actual check values exceeded these criteria; however the failure of this check was not considered critical. Table 4-2 summarizes the results of these checks. As noted in Section 4.4, the THz system checks did not meet this DQI.

The failure of the system check was not considered concerning or impactful. The empty air-space sensor measurement was made before and after each sample measurement. These empty air-space values are critical to a THz ToF measurement similar in the manner that tare weight measurement are critical to determine addition weight in a gravimetric balance test. If these air space measurements were inconsistent, then the system check was devised to help determine the source of the inconsistency, whether control unit or external reference structure. The empty air-space measurements proved consistent, indicating that the system and the external reference structure were stable, and the system check devised for this trial, however, proved inconsistent. These findings indicated that the system check method was flawed but this did not impact the testing as the empty air-space measurements were consistent. The value of the system check was never to be used in the calculation of any measurement parameter, thus the inability to hold specification does not affect the measurement results.

Table 4-2. THz Mid-Day System Checks vs. Daily Initial Set-up Values[a]

Date/Time	Initial Signal (ps)	Mid-check Signal (ps)	THz Location	Difference (ps)
Feb 16, 2011 /	80.210		Production	
Feb 16, 2011 / 16:27		80.305	Production	0.094
Feb 16, 2011 / 18;51		80.282	Production	0.072
Feb 23, 2011 / 07:50	80.187		Production	
Feb 23, 2011 / 15:05		80.200	Production	0.013
Feb 23, 2011 / 17:50		80.277	Laboratory	0.090

a – Shaded cells indicate those measurements were not made at that time.

THz Off-Sheet Air Space (Blank) Drift. Prior to each production line or laboratory test sample, a 5-second reading was collected by the THz sensor to establish the baseline ToF with no sample in the beam path. Once sample measurements were complete, a 5-second reading was collected. The QAPP acceptance criteria for the difference between the pre-and post-testing off-sheet optics checks was < $\pm 50^{-15}$ sec. The average of these two values was subtracted from each sample reading as the baseline ToF value. Table 4-3 summarizes the results. The results from all tests but one were within the acceptance criteria, with the maximum drift less than $\pm 5^{-15}$ seconds (0.005 ps).

Table 4-3. Summary of THz Air Space Samples

Sample	Production (ps)			Laboratory (ps)		
	Initial	Final	Difference	Initial	Final	Difference
Mid-Weight Paper						
ACA11B16026	Missed	260.917	*	260.908	260.905	0.003
ACA11B16027	260.919	260.918	0.001	260.904	260.903	0.001
ACA11B16028	260.950	260.920	0.030	260.902	260.902	0
ACA11B16035	260.910	260.913	0.003	260.902	260.903	0.001
ACA11B16037	260.912	260.909	0.003	260.901	260.900	0.001
Heavy-Weight Paper						
ACA11B23035	259.808	259.804	0.004	260.779	260.781	0.002
ACA11B23036	259.805	259.804	0.001	260.852	260.853	0.001
ACA11B23042	259.798	259.801	0.003	260.780	260.781	0.001
ACA11B23043	259.800	259.799	0.001	260.780	260.779	0.001
ACA11B23044	259.799	259.800	0.001	260.779	260.778	0.001

4.3 Audits

Two types of audits were performed during the verification test: a technical systems audit (TSA) of the verification test performance and an audit of data quality (ADQ). Audit results are discussed below.

4.3.1 Technical Systems Audit

The Battelle Quality Manager, Rosanna Buhl, performed a technical systems audit (TSA) at the Appleton Paper Plant during the production line and static laboratory testing of both mid-weight (February 16-17, 2011) and heavy-weight paper (February 23, 2011) verification tests. The purpose of this audit was to:

- Evaluate verification testing of the Picometrix Terahertz (THz) system to determine basis weight in an actual paper production environment with in-line nuclear gauges;
- Evaluate verification testing of the Picometrix Terahertz system to determine basis weight in the laboratory vs. Appleton and TAPPI procedures;
- Verify that temperature and relative humidity conditions in the laboratory met Appleton and TAPPI requirements;
- Review calibration records of laboratory equipment (balance, temperature and relative humidity monitor); and
- Verify that testing was compliant with QAPP requirements and that the required documentation was being completed in real time to ensure data traceability.

The TSA consisted of observations of vendor technology operation and Appleton staff performing routine procedures for laboratory and production line performance monitoring. A TSA checklist was used to guide the audit. Procedures reviewed included set-up, calibration, and testing using the THz system in the production area and laboratory, laboratory basis weight measurements, laboratory equipment readings and calibration records. Four significant TSA findings were identified.

- **Relative Humidity:** The relative humidity (RH) conditions in the TAPPI room during laboratory testing at Appleton were not maintained at the 50.0%±2.0% range specified in the QAPP DQI Table 2. Actual RH values, measured using the Hobo monitor, ranged from 41 – 47%.
- **THz Calibration:** The QAPP states that the mid-day THz checks should be $\pm 20^{-15}$ seconds vs. the initial calibration. The mid-day checks did not achieve this criterion. (Picometrix staff indicated that the term “initial calibration” was a misnomer; a more accurate term would be initial set-up to optimize the signal).
- **Production On-line Testing THz Calibration Check:** The THz system time measurement calibration was not checked on the day that laboratory static testing was performed on the mid-weight paper.
- **Sample Design:** The laboratory measurements of the heavy-weight paper did not follow the sample design. Rather than 12 pieces of paper in eight stacks measured by the THz during laboratory testing, 6 pieces of paper in 12 stacks were measured.

The remaining observations noted documentation errors and issues that would not impact data quality. A TSA report was prepared, and a copy was distributed to the EPA.

Details on how the THz sensor calibration and sample design findings were addressed are described in Section 4.4 in Deviations 2 and 4, respectively. Relative humidity information as recorded by the HOBO was provided in the report, with those values outside of the specified range highlighted. Battelle does not believe that these values impacted the study or data quality.

The production on-line testing THz sensor calibration test was not checked due to a misunderstanding by the Picometrix operator. It was determined in consultation with the vendor that this missed calibration test did not impact the performance of the THz sensor or the resulting data. All empty air space measurements were consistent. See Deviation 2 in Section 4.4 for further details.

4.3.2 Data Quality Audit

The Battelle Quality Manager audited at least 25% of the sample results data acquired in the verification test and 100% of the calibration and QC data versus the QAPP requirements. One audit of data quality (ADQ) was conducted for this project encompassing the review of raw data, synthesized data and the verification report. The ADQ was initiated within 10 business days of receipt by the Quality Manager and assessed using a project-specific checklist. During the audit, the Battelle quality manager, or designee, traced the data from initial acquisition (as received from the Appleton or the Picometrix technology), through reduction and statistical comparisons, to final reporting. Data underwent a 100% validation and verification by technical staff (i.e., Verification Test Coordinator (VTC), or designee) before it was assessed as part of the ADQ. All QC data and all calculations performed on the data undergoing the audit were checked by the Battelle Quality Manager or designee. Results of the ADQ were documented using the checklist and reported to the VTC and EPA within 10 business days after completion of the audit.

The ADQ resulted in two findings and one observation. One finding noted that deviations (as described in Section 4.4) noted in the TSA needed to documented in the report and submitted for approval. The second finding noted that various calculation errors were found in the spreadsheets used for data analysis. The observation indicated that a discussion of data completeness for the mid-weight paper roll should be included in the report. All findings and observations were addressed and corrected appropriately.

4.4 Deviations

Four deviations were documented during testing:

Deviation 1 (2-16-11): Testing and data collection began for the Verification of Picometrix, LLC, T-Ray®™ 4000 Time-Domain Terahertz System before the QAPP was approved by the EPA AMS Center Project Officer (PO). The QAPP was approved on 3-22-11. Impact: Battelle believes that this did not impact the data quality of the test. The changes to the QAPP did not include any items that would impact the test design or data collection.

Deviation 2 (2-16-2011): The QAPP states that the mid-day THz checks should be $\pm 20^{-15}$ seconds vs. the initial set-up that optimizes the THz signal. The actual values are reported in

Table 4-2 (Section 4.1.2). Impact: Battelle believes that the checks exceeding the specification did not impact the measurement results. The test was devised for this trial to help determine the source of variation, whether control unit or external reference structure, if the external reference structure empty air-space measurements were not stable. The air-space checks were very stable, thus the system and the external reference structure must have been stable. The result of the system check was never to be used in the calculation of any measurement parameter.

Deviation 3 (2-16-2011): The QAPP states that data from the first run of each paper weight (mid-weight or heavy-weight) should be used to temporarily calibrate the THz sensor to provide real-time results for subsequent measurement runs. However, the production process and schedule made this approach impractical. Rather, all data were collected electronically by the THz data system and were post-calibrated against the laboratory basis weight data. Impact: Battelle believes that this did not impact the data quality of the test. The initial plan would only have provided interim basis weight data and generation of final data were not impacted.

Deviation 4 (2-16-2011): The QAPP states that 12 pieces of paper in eight stacks would be measured by the THz during the off-line phase of the test to determine basis weight. However, for the heavy weight paper, 16 stacks with 6 pieces of paper were measured. The total number of pieces of paper measured (96) was not changed but the stack size varied. This deviation was necessary due to the thickness of the heavy weight paper (3 mm) which created a lot of noise and outliers in the THz scan. Impact: Battelle believes that this did not impact the data quality of the test. The total number of paper pieces tested was the same and thus still represents the same sample area.

Deviation 5 (9-26-2011): The QAPP states that two audits of data quality (ADQ) would be conducted. An initial ADQ was to be conducted on the on-site collected data within 10 business days of receipt by the Quality Manager. A second ADQ was to be collected on synthesized data and verification report. Because of the significant data reduction required to analyze the data the VTC and Quality Manager agreed that it was more practical to conduct one combined audit. Battelle believes that this did not impact the data quality of the test.

Chapter 5
Statistical Methods

The statistical methods used to evaluate the quantitative performance factors listed in Section 3.5 are presented in this chapter. Qualitative observations were also used to evaluate verification test data.

5.1 Accuracy

The accuracy of the results was assessed by calculating the percent error between the laboratory measurements and the results from the offline THz technology readings. Percent error was calculated using the following:

$$\%Error = \frac{\left|Technology - Lab\right|}{Lab} \times 100 \tag{1}$$

It should be noted that the laboratory measurement used for comparison in the accuracy statistic was not without some measurement error itself, as was the THz sensor. As such, the difference between the laboratory and THz measurement includes errors from both of these measurements.

5.2 Precision

The precision was calculated as the standard deviation of repeated measurements made by the THz technology during laboratory testing using the following equation:

$$StdDev = \sqrt{\frac{\sum_{i=1}^{N}\left(Xi - \overline{X}\right)^2}{\mathrm{N - 1}}} \tag{2}$$

5.3 Comparability

Comparability between the technologies was assessed by calculating the percent difference between the measurements made by the THz technology and the nuclear gauge while in the on-line production mode. This evaluation helped in assessing the performance of the THz technology in relation to that of the instrument typically used for production control processes (i.e., the nuclear gauge). Percent difference was calculated using the following:

$$\%Difference = \frac{(Terahertz\ Technology\ Result - Nuclear\ Gauge\ Result)}{Nuclear\ Gauge\ Result} \times 100 \qquad (3)$$

Comparability results were calculated for each run evaluated during the verification test. A paired t-test was used to determine if the percent difference between technology readings for a given roll of paper were significantly different from zero.

Chapter 6
Test Results

The results of the verification tests of the Picometrix T-Ray 4000® TD-THz System are presented below for each of the performance parameters.

Raw THz ToF data were processed to generate basis weight values as described below. This process was devised by Picometrix and is how they normally process similar data. The measurement of interest was the "weight" of a continuously manufactured sheet material. The factor chosen was the basis weight. Basis weight is the weight of a prescribed area sample. A common example is grams per square meter (g/m^2 or gsm). For the paper industry, the units used are pounds per ream (lb/ream) of paper. For these samples, a ream is 3,300 square feet of paper.

The THz measurement of interest was the ToF for the THz pulse to travel through the sample and be reflected back to the sensor. The ToF value, in ps, was the "raw" THz output value. This value was calibrated against accepted values of basis weight for the sample under study. The THz system used to make measurements in this study collected data at a 100 Hz rate (i.e., system collects 100 data points per second).

The nuclear gauge used in this test measured the number of beta particles (electrons) passing through the sample, indicating beta particle flux. Numerous factors affect the transmission of beta particles through materials, including but not limited to the thickness, density, and water content of the material. The beta particle flux values are calibrated to accepted values of basis weight for standard test materials. The nuclear gauge used for this testing output data at a 0.2 Hz rate (i.e., system collects one data point every five seconds).

It should be noted that cross sheet scanning was typically performed by the nuclear gauge during production at the Appleton facility. The scanning was required to monitor the uniformity of the coating process. As the nuclear gauge scanned across the sheet, the product was divided into a number of cross direction "bins". The nuclear gauge scans across the web at approximately 6 inches per second, producing 96 bin measurements for each single 15 second scan across the product. Then, a number of repeated scans were averaged before a measurement result for that bin was reported. This means for routine operation of a nuclear gauge, a single bin measurement was an average of a number of sets of measurements with each individual measurement covering a certain amount of product. These values were running averages. These average results were then reported through the system to help monitor the production process. The averaging of both across the sheet (cross direction) measurements and along the production direction (machine direction) measurements was used to maintain controlled measurement feedback to the coating devices. However, for this test, the gauges must remain in "parked" mode. Thus, the cross web averaging cannot be accomplished. However, the data acquired during this test was the closest approximation to the typical operation of the nuclear gauge and THz sensor in a controlled setting.

To generate THz basis weight values, 100 THz data points were averaged to provide measurements at a 1 second rate. The nuclear gauge values were accepted as accurate, and the 1 second increment THz ToF values were calibrated to the nuclear gauge basis weight (pound per ream of paper) values. This operation was conducted as follows.

1) A single THz ToF to nuclear gauge basis weight calibration factor (units of lbs/ream/ps) was found for each data set. This was done by finding the average nuclear gauge basis weight value, the average THz ToF value over the two entire data sets and then simply finding the ratio of these two values.
2) The five individual data sets calibration factors were then averaged to generate a single calibration factor for each sample type.
3) Using this single calibration factor, the reverse process was carried out for which the 1 second increment basis weights were recalculated for each THz data set. The results reported are the measurement time (1 second increment), associated nuclear gauge basis weight measurement (if it existed), the "raw" THz ToF measurement (if it existed) and the THz calculated basis weight.

These THz basis weight values were then used for the calculations described in the following sections.

The THz data were also examined for outliers during processing. The THz errant readings are most often caused by an incorrectly assigned finding when determining the time and amplitude of the waveform pulses. As multiple outliers were possible, a Grubb's t-test was used to determine outliers. First the mean and standard deviation were calculated (X_{bar} and s). Then, starting with the largest outlier, T was calculated, where

$$T = \frac{|X_i - X_{bar}|}{s}$$

If $T > 3.017$, then X_i was rejected. That is, that result was regarded as an outlier and removed from the data set. Then X_{bar} and s were recalculated from the remaining data and the Grubb's t-test was used to determine the next largest outlier. Some outliers were found in the THz datasets. In any instance, less than 0.1% of the data (30 out of 30,000 measurements) was considered to be outliers through this process.

6.1 Accuracy

Accuracy was assessed by comparing the results from the measurement of basis weight using the TAPPI gravimetric reference method to the offline (laboratory) THz basis weight measurements on tear-off samples from the end of each roll of paper evaluated in the verification test. Both gravimetric and offline THZ measurements were made in the temperature and humidity controlled TAPPI room. The results of the two basis weight measurements were compared by evaluating the percent error between the laboratory results and offline THz results. Table 6-1 summarizes the accuracy of offline THz basis weight data compared to the TAPPI gravimetric reference method.

The percent error for the THz basis weight, as compared to the laboratory gravimetric reference method values, ranged from 0.1-2.8% for the mid-weight rolls and 0.3-2.9% for the heavy-weight rolls. The percent error for the offline THz sensor readings, based on the averages across all five rolls for a particular weight paper, was 0.02%. The average percent error for a mid-weight ream measurement, calculated as the average of all of the mid-weight paper percent errors presented in Table 6-1, was 1.4%, significantly higher than the average across all five rolls. The average percent error for a heavy-weight ream was similar at 1.3%.

The standard deviations of the average laboratory gravimetric measurements as well as the THz offline basis weight measurements are also provided in Table 6-1 for each paper weight. The standard deviation of the mid-weight paper basis weight for the offline THz sensor results was 0.64 lb/ream. This was similar to the standard deviation of the laboratory gravimetric reference method basis weight measurements across all five mid-weight paper rolls (0.56 lb/ream). The standard deviations across all heavy weight paper rolls varied between the measurement techniques. The standard deviation for the THz heavy weight measurements was approximately twice that of the laboratory values. According to the vendor, typical standard deviations expected for the THz technology generally range from 0.1% to 0.2%. It was determined after the verification test that the design of the offline THz measurements may not have been ideal and might explain the higher than expected standard deviation found for the THz offline results. This is discussed further in the next section (Section 6.2).

Table 6-1. Accuracy of THz Basis Weight Values vs. Standard Laboratory Measurements.

Sample ID	Laboratory Gravimetric Basis Weight (lb/ream)	THz Basis Weight (mean ± Std)	THz Basis Weight % Error	% THz to Laboratory Basis Weight
Mid-Weight Paper				
ACA11B16026	50.05	49.59	0.9%	99%
ACA11B16027	49.83	48.58	2.5%	97%
ACA11B16028	48.77	50.15	2.8%	103%
ACA11B16035	50.02	50.06	0.1%	100%
ACA11B16037	49.57	49.93	0.7%	101%
Average	**49.65**	**49.66**	**0.02%**[a]	**100%**
STD	**0.56**	**0.64**		
Heavy Weight Paper				
ACA11B23035	157.25	156.66	0.4%	100%
ACA11B23036	157.54	152.96	2.9%	97%
ACA11B23042	157.01	158.36	0.9%	101%
ACA11B23043	155.00	158.44	2.2%	102%
ACA11B23044	156.05	156.59	0.3%	100%
Average	**156.57**	**156.60**	**0.02%**[a]	**100%**
STD	**1.04**	**2.22**		

a – Average percent error based on percent error of average basis weight measurements, not average of all percent error calculations.

6.2 Precision

The precision of the THz technology was assessed on offline replicate measurements made on cut samples of heavy weight paper. Triplicate measurements were made on one stack of heavy weight paper. The results are summarized in Table 6-2. The standard deviation was 0.0115 ps across the replicate measurements with a coefficient of variation of <0.005%.

Table 6-2. Precision of Replicate THz Readings

Sample ACA11B23035	THz Results (ps)
Rep 1	266.917
Rep 2	266.917
Rep 3	266.897
Average	**266.910**
STD	**0.0115**
Coefficient of Variation	**0.0043%**

The vendor noted that, based on experience and past-performance of the technology, that the accuracy and precision of the laboratory THz basis weight measurements and replicated THz readings were higher than expected (by approximately 20x). A review of the laboratory testing method revealed a flaw in the test design used that likely led to these higher-than-expected offline THz results.

As noted in Section 3.2.2, the paper sample size for the gravimetric analysis was four precisely cut 9.5 x 12.5 inch squares, creating a 475 square inch sample. When developing the test plan for the offline THz measurements, two main concerns were taken into consideration. First, that the THz measurements needed to be taken over a set of points well distributed across the 475 square inches. Second, that the normal spatial variability in basis weight of the paper (i.e., its formation) will require a large number of THz measurements to eliminate this variability.

The offline THz measurement procedure followed was to cut the entire sample into 96 four square inch (2 inch by 2 inch) pieces. These individual pieces were then stacked into groups of 8 or 16 and the THz ToF was measured for the whole stack. The theory was that the stacking of samples would randomize the sample's basis weight variation and speed the measurement process.

This measurement method was dependent on the positioning, curvature and spacing between the sample sheets. The variation in these parameters generated an unintended significant variation in the ToF measurement results. The assumption was that the main THz pulse would pass through the stack, reflect off the external reference structure (ERS) rear surface and pass back through the stack. In this configuration, the measurement of this "first light" main pulse would represent the total delay through the stack. The vendor indicated that the main pulse behaved as expected.

However, upon analyzing the data, the vendor explained that because of variations in the positioning, curvature, and spacing between the sheets of paper in the stack, a very large number of small amplitude peaks (<5%) also occur due to reflections between the sheets of paper of the stack (see Figures 6-1 and 6-2).

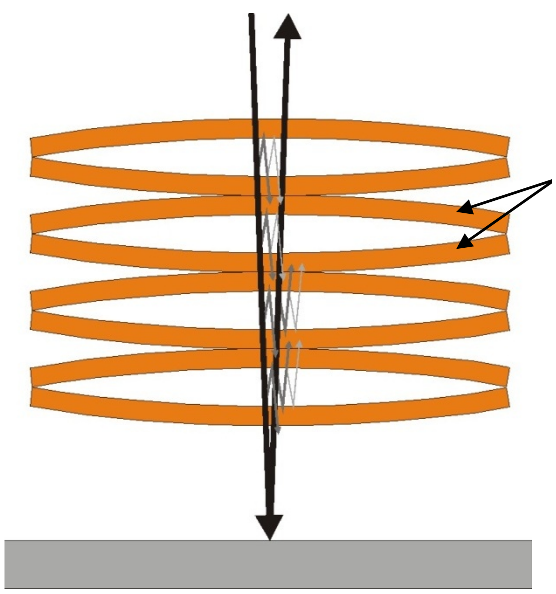

Figure 6-1. Laboratory sample measurement method

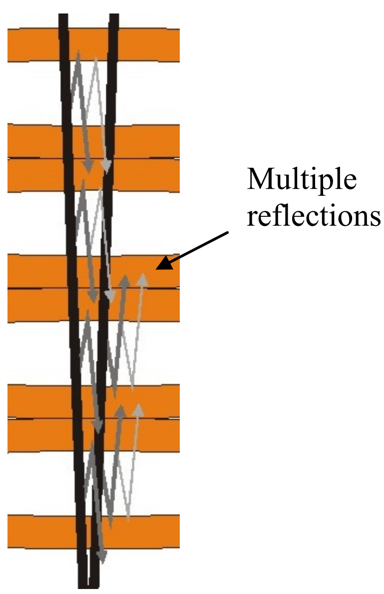

Figure 6-2. Zoom on multiple reflections from paper sheet samples

These reflections always originate from the main pulse, thus they always will be present *after* this main pulse. These small amplitude reflection pulses become convolved with the trailing edge of the main pulse. Thus, this inter-sample sheet reflection changed the shape of the pulse. In order to determine a reflection pulse ToF value, the entire pulse, typically around 4 ps was used. Thus, changes in the trailing edge of the pulse will affect the measurement of the pulse's time-of-flight. The vendor indicates that these changes will be variable, depending on the configuration of the stack of the individual sheets. Curved samples, like paper, will exhibit more variability.

Because stacks of paper were used, the vendor believes that this testing procedure affected the laboratory THz basis weight measurements, resulting in a reduction in the accuracy and precision of the laboratory stacked paper testing results. In retrospect, the vendor indicated that a more robust measurement method would have been to cut the gravimetric samples into strips and drag a single strip through the measurement spot while collecting continuous data. By cutting strips throughout the sample, the desired spatial coverage would have been achieved.

6.3 Comparability

The comparability of the THz to the nuclear gauge was assessed by evaluating the online THz basis weight results against the online nuclear gauge basis weight results. An initial exploratory analysis was performed by plotting the basis weight results for each technology to determine how well the online basis weight values track each other.

Figures 6-3 – 6-7 show the THz and nuclear gauge basis weight data plotted together for each roll of mid-weight paper roll. The Y-axis scale spans 1 – 1.5 lbs/ream for the midrange products. Figures 6-8 – 6-12 show the THz and nuclear gauge basis weight data plotted together for each roll of heavy weight paper. The Y-axis scales span 3.5 – 5.5 lbs/ream for these products. These data represent all of the THz and nuclear gauge data collected during the production line testing. As noted previously, the THz data shown in each figure were averaged to provide measurements at a one second rate. The nuclear gauge data are at a frequency of once every five seconds. For Figures 6-3-6-12, the red data represent the nuclear (beta) gauge results and the black data represent the THz sensor results.

As noted in Section 3.5.3, a factor limiting the comparison between the nuclear gauge and THz sensor was the difference in measurement spot size between the two technologies. A typical nuclear gauge inspection spot was 25 millimeter (mm), while a typical THz sensor inspection spot was 2 mm. At a production line speed of 4000 feet/minute, these "spots" become spread to 25 mm x 1041 mm for the nuclear gauge's 50 millisecond measurement integration time and 2 mm x 125 mm with an 80 mm gap between THz measurements. Thus, these two systems inspected the product in different ways. The nuclear gauge covered a larger area and thus could provide an improved result for the average basis weight value. The higher measurement rate of the THz system somewhat compensated for this difference. In addition, the smaller THz sensor inspection spot allows for better streak detection and could possibly provide information on the formation (uniformity of basis weight) of the sample.

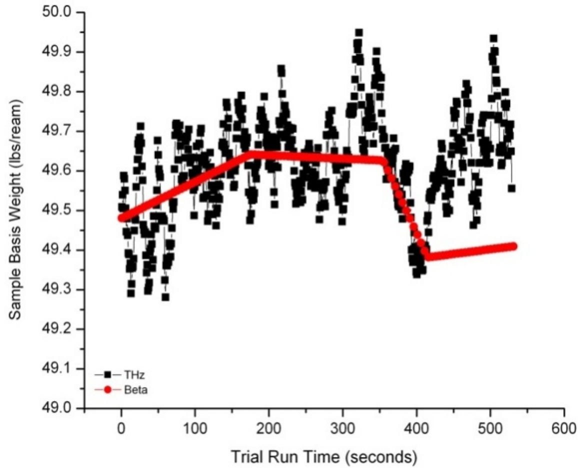

Figure 6-3. ACA11B16026 on-line results.

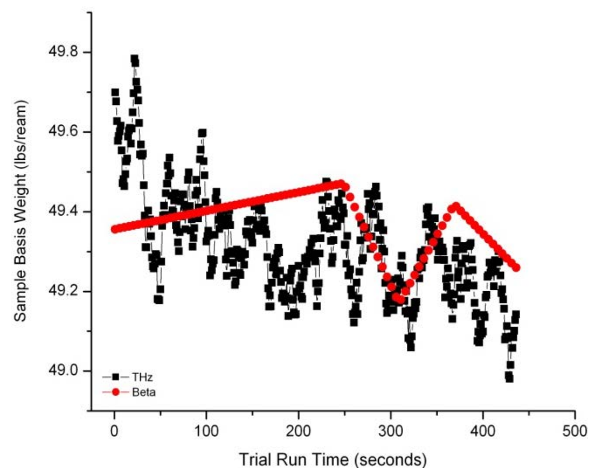

Figure 6-4. ACA11B16027 on-line results.

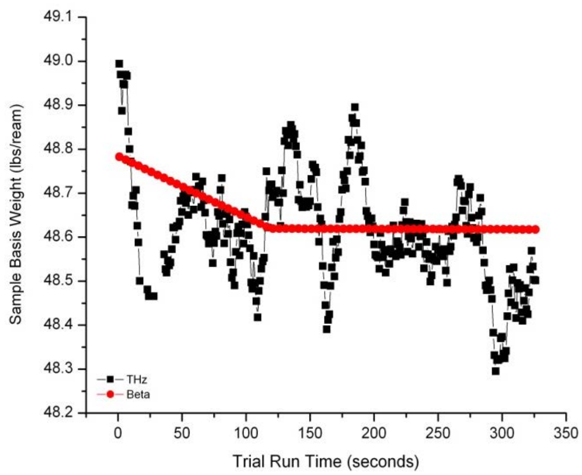

Figure 6-5. ACA11B16028 on-line results.

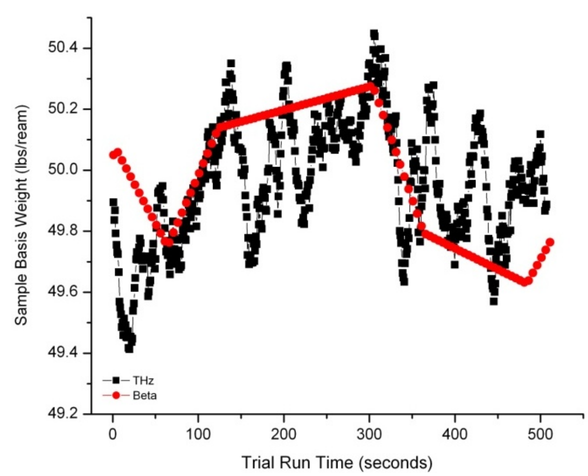

Figure 6-6. ACA11B16035 on-line results.

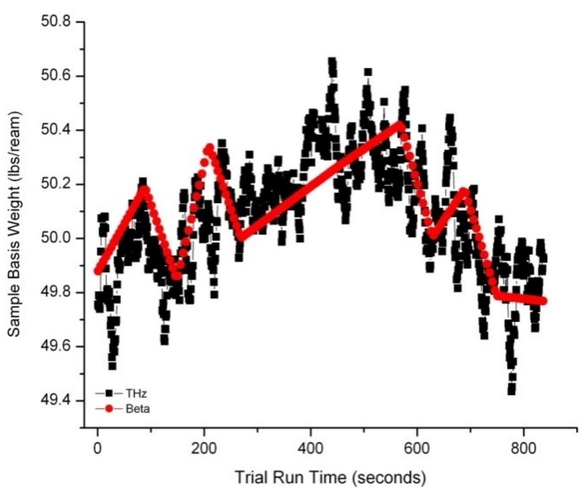

Figure 6-7. ACA11B16037 on-line results.

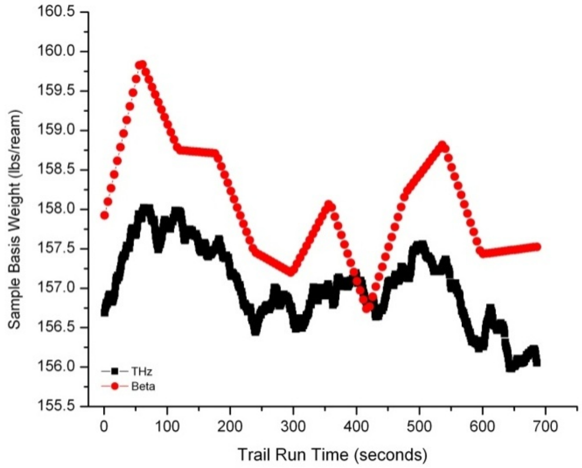

Figure 6-8. ACA11B23035 on-line results.

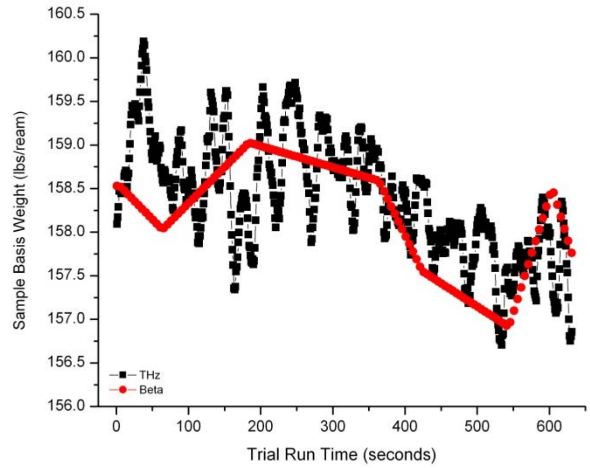

Figure 6-9. ACA11B23036 on-line results.

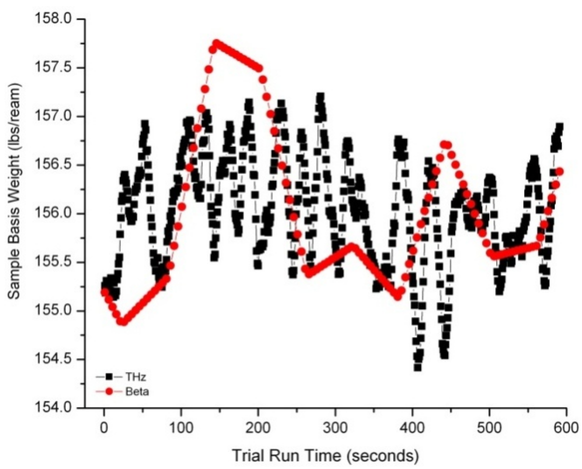

Figure 6-10. ACA11B23042 on-line results.

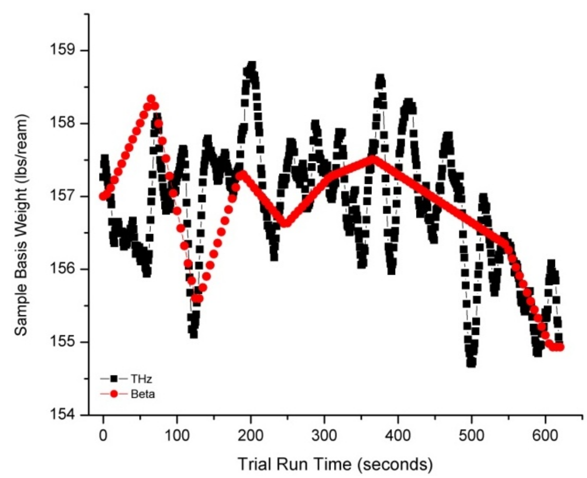

Figure 6-11. ACA11B23043 on-line results.

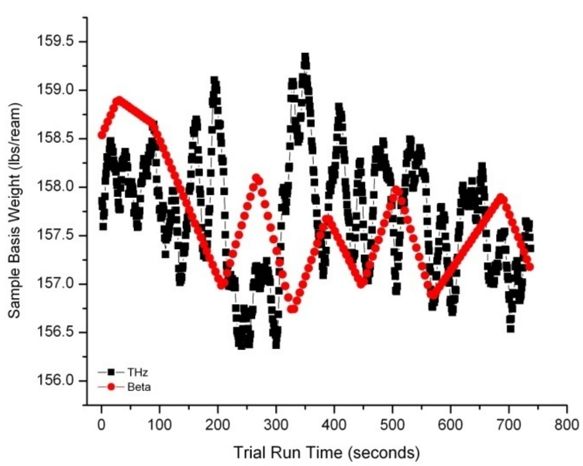

Figure 6-12. ACA11B23044 on-line results.

Of note is the less-varied, more piece-wise linear fit appearance of the production nuclear gauge measurements. Appleton expressed surprise that the nuclear gauge data appeared as linear and smooth as shown in Figures 6-3 through 6-12. It was suggested that this was a result of some filtering on the nuclear gauge results. Note that the nuclear gauge does not normally operate in a parked position as was used in the verification test. This filtering introduces a significant change in the "shape" of the production basis weight that was useful for production needs but, according to Appleton, does not represent the actual second-by-second basis weight values. Unless the THz measurements are filtered in the same manner, this change will introduce some error in the quantitative comparison between the two data sets. The Appleton staff did not know the exact filtering used on the nuclear gauge online basis weight data. Thus, it was determined that the THz data would be treated with a relatively weak filter, an 11 point adjacent average, to attempt to match the gross features of the nuclear gauge data. Thus, the THz results are presented in a less processed manner to better illustrate the sensor's "real time" measurement capabilities. Picometrix has indicated that the results can be further processed to introduce the necessary damping needed for production feedback control.

As shown in Figures 6-3 through 6-12, in most cases, the THz data track the nuclear (beta) gauge results well, following the trend of the nuclear gauge data. There are some instances, however, where the data diverge. For the mid-weight paper, Figure 6-3 shows that the THz basis weight measurements show a steeper rise at around 400 seconds while the nuclear gauge results rise at a slower rate. Figure 6-4 also shows a slight divergence, with the nuclear (beta) gauge basis weight values rising slightly while the THz results fall slightly at the beginning of the roll.

For the heavy weight paper, Figures 6-8 and 6-10 show divergence between the results of the two technologies. In Figure 6-8, the overall trends in basis weight results are similar for both technologies. However, the THz results are consistently lower than the nuclear gauge results. In Figure 6-10, the nuclear gauge basis weight values peak noticeably around 100 seconds while the THz values do not show such a change.

It is important to note that the y-axis was generally on a small scale and that the differences being viewed are small in magnitude. For example, the offset between the basis weight results in Figure 6-3 when the THz sensor results rise faster than the nuclear gauge results was approximately 0.2 lbs/ream. The offset in Figure 6-8 was larger, closer to 1-2 lbs/ream.

To further explore the comparability between the THz and nuclear gauge production line measurement results, especially quantitatively, the percent difference between paired measurements for each technology on each roll of paper were evaluated. As noted previously, the THz sensor recorded measurements significantly more frequently than the nuclear gauge and were averaged during data preparation such that there were five THz measurements to every one nuclear gauge measurement. These data were then used for pairing the nuclear and THz sensor results. For these comparisons, the THz observation times were rounded to the nearest integer and matched to the corresponding nuclear gauge times. This was accomplished using Excel's VLOOKUP feature. In cases of ties, VLOOKUP captured the earliest observations of the two. The percent difference was then calculated for each matched pair of THz and nuclear gauge production line data.

Figures 6-13 through 6-32 show the percent difference between the THz and nuclear gauge results for each roll of paper evaluated. For each production roll, two figures highlight the percent difference between the THz and nuclear gauge results. One figure is a function of point-by-point percent difference for the entire trial run time, based on the matched pairs discussed above. The second figure is a histogram of the same percentage difference results. In the histograms, the percent difference results for a particular roll of paper are binned together in 0.1% difference increments and show the varying amounts of levels of percent difference within the given roll of paper.

Figures 6-13 – 6-22 present results for the mid-weight rolls and Figures 6-23 – 6-32 are for the heavy weight rolls. Note that in most cases, the histogram has Gaussian shape with the peak centered on 0% difference. Many of the histogram figures, however, appear flattened which was likely due to the comparison of the THz results and the forced linear fit sections of the nuclear gauge values. The percent difference for the heavy weight roll ACA11B23035 shows a consistently negative percent difference, highlighting the consistent offset of the THz and nuclear gauge results shown in Figure 6-8. Note that in all cases, the percent difference was <2% for the basis weight measurements by these two technologies. In fact, for many cases, the percent difference was <1%. All percent differences were well below the 10% specified in the QAPP.

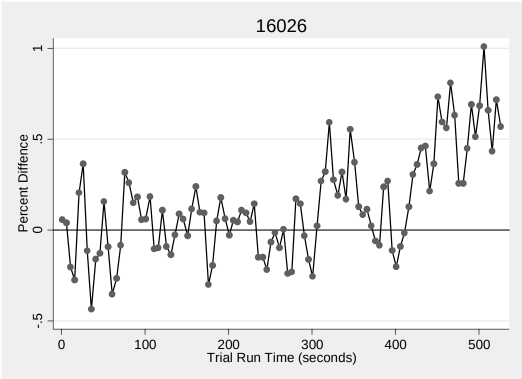

Figure 6-13. ACA11B16026 Percent Difference Trial Run Time

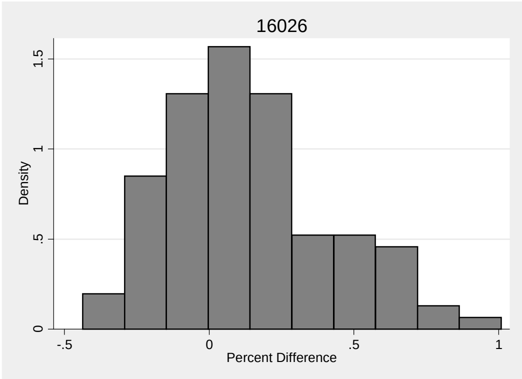

Figure 6-14. ACA11B16026 Percent Difference Histogram

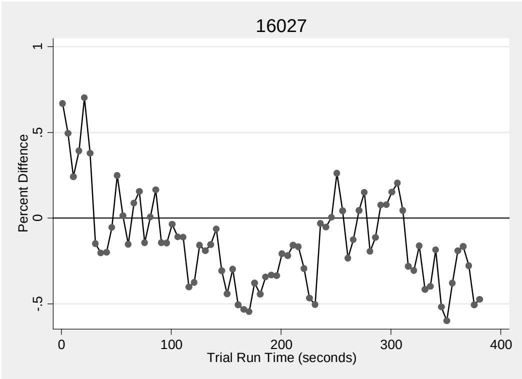

Figure 6-15. ACA11B16027 Percent Difference Trial Run Time

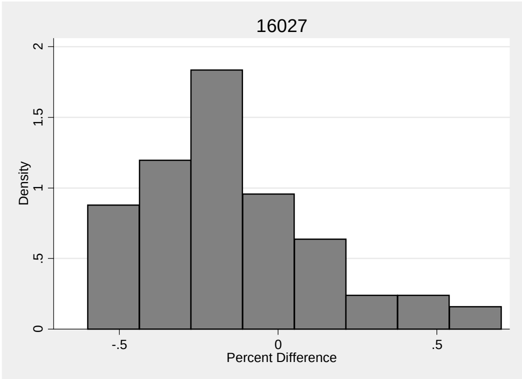

Figure 6-16. ACA11B16027 Percent Difference Histogram

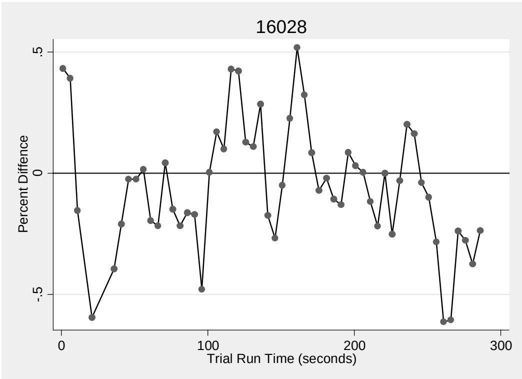

Figure 6-17. ACA11B16028 Percent Difference Trial Run Time

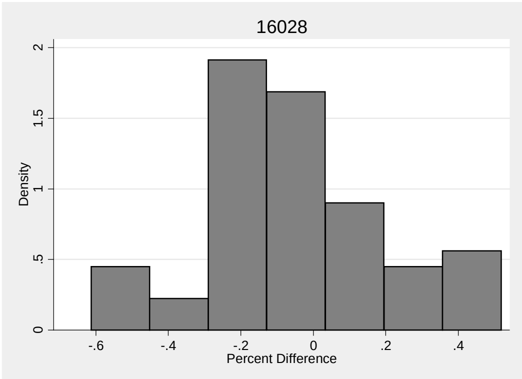

Figure 6-18. ACA11B16028 Percent Difference Histogram

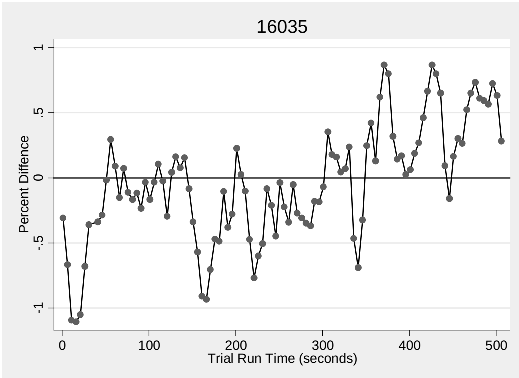

Figure 6-19. ACA11B16035 Percent. Difference Trial Run Time

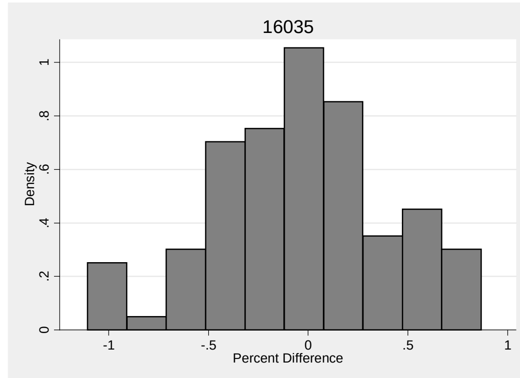

Figure 6-20. ACA11B16035 Percent Difference Histogram

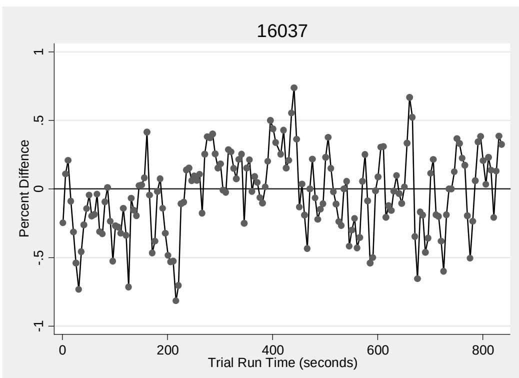

Figure 6-21. ACA11B16037 Percent. Difference Trial Run Time

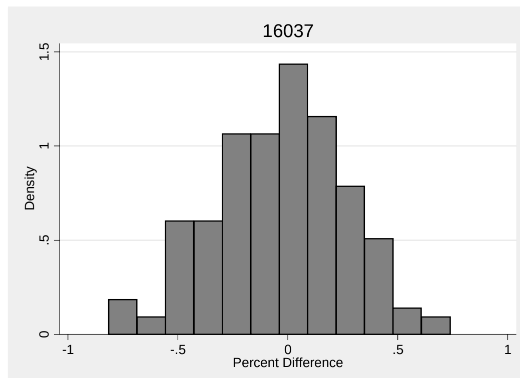

Figure 6-22. ACA11B16037 Percent Difference Histogram

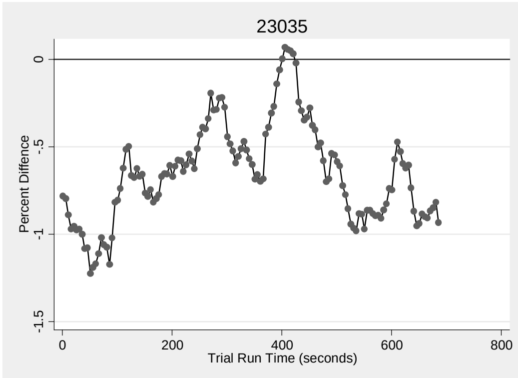

Figure 6-23. ACA11B23035 Percent. Difference Trial Run Time

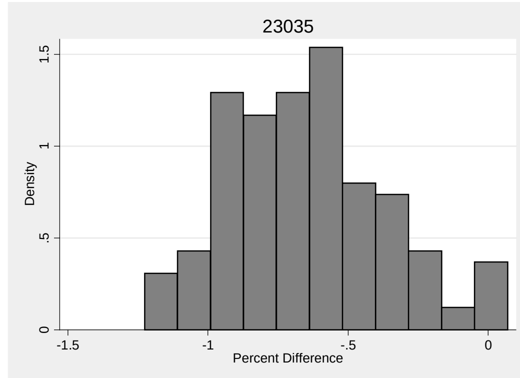

Figure 6-24. ACA11B23035 Percent Difference Histogram

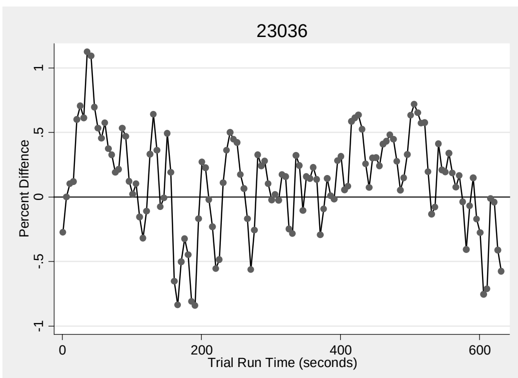

Figure 6-25. ACA11B23036 Percent Difference Trial Run Time

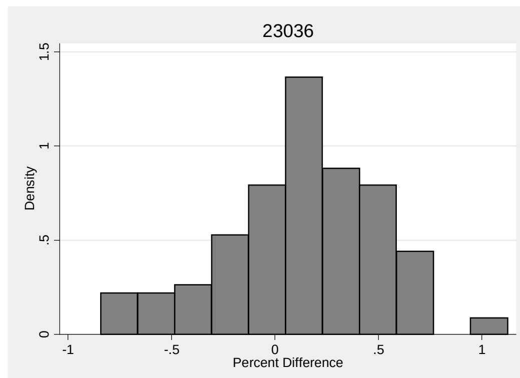

Figure 6-26. ACA11B23036 Percent Difference Histogram

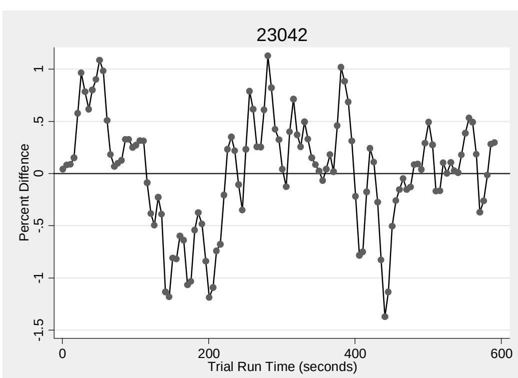

Figure 6-27. ACA11B23042 Percent. Difference Trial Run Time

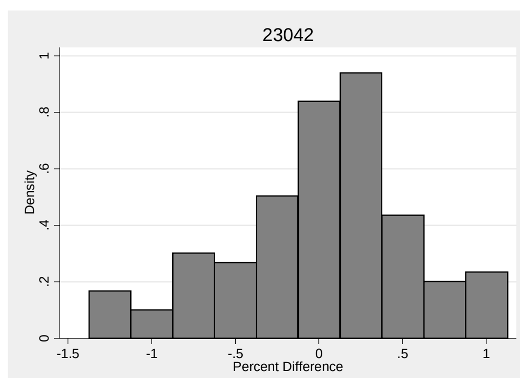

Figure 6-28. ACA11B23042 Percent Difference Histogram

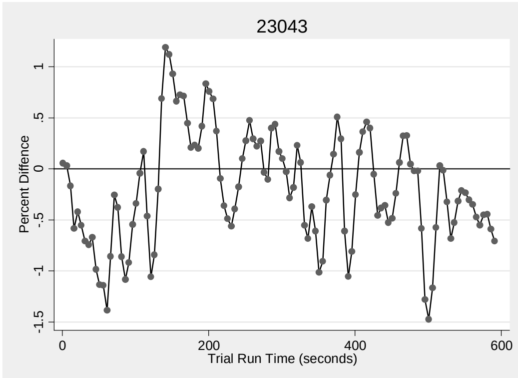

Figure 6-29. ACA11B23043 Percent Difference Trial Run Time

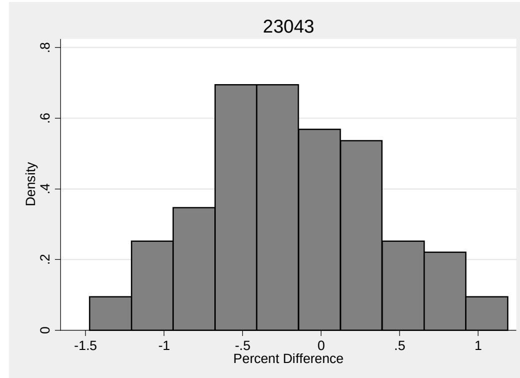

Figure 6-30. ACA11B23043 Percent Difference Histogram

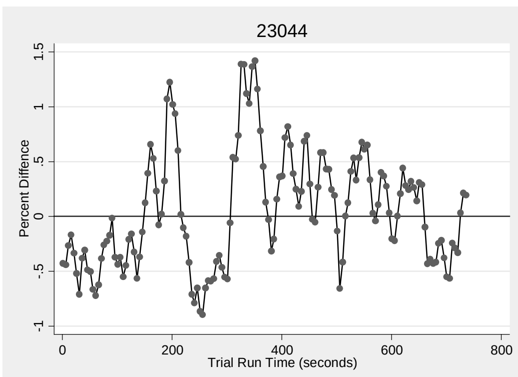

Figure 6-31. ACA11B23044 Percent Difference Trial Run Time

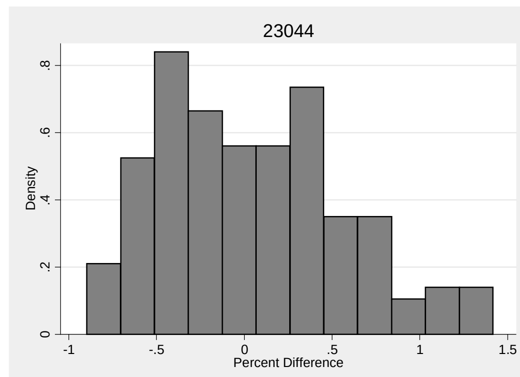

Figure 6-32. ACA11B23044 Percent Difference Histogram

The average basis weight value for each roll of paper as measured by the THz and nuclear gauge technologies along with the average percent difference for each roll is provided in Table 6-3. Standard deviations of each mean are also presented. The mean percent difference was calculated by averaging the percent difference for each roll. To evaluate whether the mean percent difference was significantly different from zero, a t-test was used.

Table 6-3. Comparison of Production Measurements Between THz and Nuclear Sensors

Roll Number	Beta Mean Basis Weight	Beta SD[1]	THz Mean Basis Weight	THz SD	Mean Percent Difference	Percent Difference SD	T-test P-value[2]
16026	49.54	0.096	49.61	0.123	0.14 %	0.282	<0.001
16027	49.38	0.072	49.31	0.131	-0.13 %	0.275	<0.001
16028	48.65	0.048	48.62	0.134	-0.06 %	0.260	0.122
16035	49.98	0.218	49.96	0.199	-0.04 %	0.449	0.429
16037	50.10	0.175	50.08	0.211	-0.03 %	0.297	0.133
23035	158.06	0.734	157.03	0.501	-0.65 %	0.283	<0.001
23036	158.20	0.625	158.39	0.686	0.12 %	0.381	<0.05
23042	156.00	0.805	156.04	0.556	0.03 %	0.542	0.567
23043	156.96	0.562	156.65	0.842	-0.20 %	0.550	<0.05
23044	157.64	0.557	157.72	0.629	0.05 %	0.527	0.210

1. SD: Standard Deviation
2. T-test of whether Mean Percent Difference is significantly different from zero. P-values less than 0.05 indicate a statistical significant difference from zero.

Overall, the variability between the nuclear gauge and THz basis weights, as indicated in Figures 6-13-6-32 and in the standard deviation columns of Table 6-3, was comparable. However, there seems to be greater variability among the nuclear gauge heavy weight roll measurements as compared to the THz heavy weight roll measurements. Roll Number 23035 shows a slight departure in measurements between the nuclear gauge and the THz. This resulted in the roll having the largest percent difference among the other rolls of -0.65%. The reason for this single production run to show a significantly larger percent difference error is unexplained.
The absolute average percent difference error for most production runs was less than 0.15%. Using the Q-test ($Q = 0.645 > Q_{99\%} = 0.568$) to reject the 23035 result as an outlier results in an average percent difference of less than 0.1% for all rolls.

For the mid-weight samples, three of the five production runs had a sufficiently high p-value ($p>0.05$) to be considered to have the statistically same mean value. Two of the five production runs for the heavy weight samples had statistically the same mean value. The mean percent difference between the nuclear gauge and THz for each roll was significantly different from zero, according to the t-test, for Roll Numbers 16026, 16027, 23035, 23036, and 23043.

Note that, because of the time series nature of the data produced during this test, the data are autocorrelated. This means that the data near in time are more likely to be similar that those far apart in time. To account for this, the data could be reduced by the interval at which they become independent and are no longer autocorrelated. This adjustment was not made in the data from this test, however, as the difference between the two technologies was very small and, regardless of the interval of data used, this relationship would still remain very small and well within the defined criteria of acceptance.

6.4 Operational Factors

Operational factors related to the THz technology were evaluated based on Battelle staff testing observations and input from Picometrix, LLC. Table 6-4 summarizes these operational factors. For the base system configured for industrial applications, the list price is $220,000.

Table 6-4. Summary of THz Operational Factors

Operational Factor	Assessment
Start-up	Factory installation, set-up and peak definition. No factory or operator actions are required after setup. Picometrix performs the setup on site. If the filter settings are accidently changed, the password will lock the user out of the system to prevent collection of erroneous data.
Ease of Use	Once set up is complete, the software protocol will prompt for product and coating stage and convert ToF to basis weight.
Clarity of Instruction Manual	Not assessed. The manual is very large and detailed.
User-friendly Software	The user interface has not yet been developed but the intent is that it will be programmed for basic use.
Conveniences	Small size, single-sided, no regulatory oversight required due to radiological concerns
Daily Status of Diagnostic Indicators	The units have diagnostics to tell if and when re-calibration is required. A warning message is displayed and transmitted to the unit.
Maintenance Needs and Level of Effort/Vendor Effort	The laser must be replaced every 5 – 10 years. The laser window must be cleaned weekly by the user.
Downtime Causes and Duration	Significant static electricity was present during the Feb 16 production runs and some occasional unexpected operation (active channel switched) was observed, mostly on the laptop computer. The instrument should be grounded when installed.
Data acquisition failure	None observed to date.
Power Supply Nature and Needs	90 – 264 volts; 47 – 63 Hz <100 watts power use No surge >320 watts
Calibration Frequency	Automatically every scan. Will go off sheet and will calibrate vs. the air gap. A NIST standard can be placed in line monthly at the user's discretion.
Data Output	Digital output in real time; pulled into time "bins" for controllers. There is a protocol to convert raw data to basis weight.
Consumable Needs/Use/Replacement	Few: Power fuses and laser
Repair Requirements	There is a diagnostics table for the customer. Units are returned to Picometrix for repair.

Chapter 7
Performance Summary

The performance of the Picometrix LLC THz sensor was verified based on accuracy, precision, comparability, and operational factors. The THz sensor was compared to a nuclear gauge for the measurement of basis weight in a production and offline, laboratory environment. Performance parameters were determined based on data obtained using two different weights of paper – mid-weight and heavy-weight.

Accuracy was assessed by comparing the results from the measurement of basis weight using the TAPPI laboratory gravimetric reference method to the offline THz sensor basis weight measurements on tear-off samples taken from the end of each roll of paper. The results of the two basis weight measurements were compared by evaluating the percent error between the laboratory and offline THz sensor results. The percent error for the THz sensor basis weight, as compared to the laboratory gravimetric reference method values, ranged from 0.1-2.8% for the mid-weight rolls and 0.3-2.9% for the heavy-weight rolls. The percent error for the offline THz sensor readings, based on the averages across all five rolls for a particular weight paper, was 0.02%.

The precision of the THz sensor was assessed on replicate measurements made on cut samples of heavy weight paper. Triplicate measurements were made on one stack of heavy weight paper. The standard deviation for these replicate THz sensor measurements was 0.0115 ps with a coefficient of variation of <0.005%. It was determined that a non-ideal testing method was used for the THz sensor offline testing which lead to a much higher than expected (~20 times) imprecision in the THz sensor results. The variability in the paper stack configuration was found to contribute to the variability in the type of THz sensor measurement undertaken in this verification test. The vendor felt that this sample position variability was significant and greatly impacted the ability to draw meaningful conclusions from the static sample laboratory tests.

The comparability of the THz sensor to the nuclear gauge was assessed by evaluating the online basis weight results against the online nuclear gauge results. Plots of these data showed that the THz sensor data tracked the nuclear gauge basis weight trends for most rolls across both paper weights. In four instances, the THz sensor basis weight results diverged at some point within the production of a roll of paper. The offset in the two data sets at these points was 0.2 lbs/ream for most rolls and 1-2 lbs/ream for one roll where there was a consistent offset between the THz sensor and nuclear gauge data. In the other three instances, the data divergence was only over the course of seconds at certain points in the production of a particular roll.

The percent difference between the mean basis weight values for the on-line THz sensor and nuclear gauge results for approximately 5 – 12 minute data runs are highlighted in Table 7.1.

The average percent difference in the mean values ranged from -0.65% to 0.14%. All but one of the mean basis weight measurements of the THz sensor and nuclear gauge technologies was within ±0.20%.

Table 7-1. Comparison of Online Production Mean Percent Difference Values for THz and Nuclear Sensors Basis Weight

Roll Number	Mean Percent Difference	T-Test P-Value	Roll Number	Mean Percent Difference	T-Test P-Value
Mid-Weight Paper			**Heavy Weight Paper**		
16026	-0.14 %	<0.001	23035	-0.65%	<0.001
16027	-0.13 %	<0.001	23036	0.12%	<0.05
16028	-0.06 %	0.122	23042	0.03%	0.567
16035	-0.04 %	0.429	23043	-0.20%	<0.05
16037	0.03 %	0.133	23044	0.05%	0.210

To evaluate whether the mean percent difference was significantly different from zero, a t-test was used. Table 7.1 lists the p-values for these t-tests. P-values less than 0.05 indicate a statistical significant difference from zero. For the mid-weight samples, three of five production runs had p-values >0.05, indicating no statistically significant difference between the means of the two. Similar statistical testing for two of the five production runs for the heavy-weight samples indicated that there was no statistically significant difference between sample means.

The nuclear gauge data were processed to provide a piece-wise linear fit response that was useful for production control. The THz sensor data were lightly smoothed to mimic this fit to some degree, but the THz sensor data still retained its more variable measurement value behavior.

Operational factors related to the THz technology were evaluated based on Battelle staff testing observations and input from Picometrix, LLC. Picometrix states that the THz sensor was approximately 50 times smaller and lighter than the nuclear gauge enclosure. The Picometrix LLC THz sensor operates on the principal of EM reflection and which makes system setup, use, and maintenance easier than for the nuclear gauge. Also, the THz system does not rely on any radiological sources and thus does not present any special safety concerns or any special procurement, use, or disposal concerns (e.g., extra disposal costs or potential exposure hazards). The laser must be replaced every 5-10 years; the laser window must be cleaned weekly, but no factory or operator actions are required after the initial vendor setup. The instrument was automatically calibrated during each scan; a NIST standard can be placed in-line monthly at the user's discretion. The THz system has diagnostics to indicate to the user if and when recalibration is required. The instrument should be adequately grounded when installed, as some occasional interruptions in operation were observed due to static electricity. The instrument requires 90-246 volt power supply and uses <100 watts of power. Data were output digitally in real-time. The unit cost is $220,000.

Chapter 8
References

1. *Quality Assurance Project Plan for Verification of Picometrix, LLC T-Ray 4000® Time-Domain Terahertz System,* Battelle, Columbus, Ohio, February 23, 2011.

2. Quality Management Plan for the ETV Advanced Monitoring Systems Center, Version 7.0, U.S. EPA Environmental Technology Verification Program, Battelle, Columbus, Ohio, November 2008.

3. Appleton Standard Test Method, "Basis Weight – Lab Determination of Coated and Uncoated Paper," Spec. No. 10001.00, Revision 1, July 1993.