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Environmental Technology Verification Report

MONITEK
TST-SC
ON-LINE TURBIDIMETER

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Environmental Technology Verification Report

ETV Advanced Monitoring Systems Pilot

Monitek TST-SC On-Line Turbidimeter

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Notice

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Foreword

The U.S. Environmental Protection Agency (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 (ORD) 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 permittees, 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. At present, there are twelve environmental technology areas covered by ETV. Information about each of the environmental technology areas covered by ETV can be found on the Internet at <http://www.epa.gov/etv.htm>.

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. In 1997, through a competitive cooperative agreement, Battelle was awarded EPA funding and support 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/07/07_main.htm.

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List of Abbreviations

| | |
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| AC | alternating current |
| AMS | Advanced Monitoring Systems |
| CU | color unit |
| DC | direct current |
| EPA | U.S. Environmental Protection Agency |
| ETV | Environmental Technology Verification |
| gpm | gallons per minute |
| LOD | limit of detection |
| NIST | National Institute of Standards and Technology |
| NPT | normal pipe thread |
| NTU | nephelometric turbidity unit |
| QA | quality assurance |
| QC | quality control |
| QMP | Quality Management Plan |
| RSD | relative standard deviation |

Chapter 1 Background

The U.S. Environmental Protection Agency (EPA) has created 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 substantially 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, permitting, purchase, and use of environmental technologies.

ETV works in partnership with recognized testing organizations; with stakeholder groups consisting of regulators, buyers and vendor organizations; 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 protocols to ensure that data of known and adequate quality are generated and that the results are defensible.

The EPA's National Exposure Research Laboratory and its verification organization partner, Battelle, operate the Advanced Monitoring Systems (AMS) pilot under ETV. The AMS pilot recently evaluated the performance of on-line turbidimeters for use in water treatment facilities. This verification report presents the procedures and results of the verification test for the Monitek TST-SC on-line turbidimeter.

Chapter 2 Technology Description

The following description of the Monitek TST-SC turbidimeter is based on information provided by the vendor.

The Monitek Technologies Monilog Model TST-SC uses on-line turbidimeter alternating four-beam technology to measure turbidity and suspended solids. This method uses an array of two light-emitting diodes (LEDs) and two detectors. The LEDs are oriented 90 degrees from each other and are pulsed alternately. This causes the two detectors (located across the process stream and 90 degrees apart) to alternate between their functions as the scatter and direct beam detectors. Since each detector element alternates between functions as the measurement and reference channel, the system compensates for variations in the LED output, window coatings, and other effects. The 90 degree angle, the correction of the ray path with lenses, and the infrared light wavelength of 875 nm meet the requirements of ISO 7027.⁽¹⁾ The lower limit of the TST-SC's response range is 0.1 NTU.



Figure 2-1. Monitek Monilog Model TST-SC On-Line Turbidimeter

Chapter 3 Test Design and Procedures

3.1 Introduction

The verification test was conducted according to procedures specified in the *Test/QA Plan for Verification of On-Line Turbidimeters*.⁽²⁾ Performance characteristics evaluated in the verification test are listed in Table 3-1, along with the dates that data were collected for these evaluations. The test was conducted at a full-scale municipal water treatment facility in Columbus, Ohio. The verification test described in this report was conducted from September 9 through October 26, 1999, as indicated in Table 3-1.

Table 3-1. Performance Characteristics Evaluated and Schedule of Verification Tests Conducted on the Monitek TST-SC Turbidimeter

| Performance Characteristic | Date Data Collected |
|----------------------------|---|
| Off-Line Phase | |
| Linearity | September 9 to 10; October 20-21 |
| Accuracy | September 9 to 10 |
| Precision | September 9 to 10 |
| Water temperature effects | September 10, 14 to 15 |
| Flow rate sensitivity | September 15 to 16 |
| Color effects | October 25 to 26 |
| On-Line Phase | |
| Accuracy | September 17 to October 18 |
| Calibration checks | September 23, 24, 27, 30 and October 6, 8, 12, 18 |

3.2 Test Design Considerations

Since turbidity is a measurement of light scattering, a number of factors can influence the measurement of turbidity in a given sample solution. Instrument design, including light source selection and geometric differences, may result in significant differences between the responses of different turbidimeters. Further differences may result from the variable nature of both the size and composition of particles typically found in water streams, relative to those in standard

solutions made with formazin or polymer beads. These issues were addressed in this verification test in two ways: (1) by using different instrumental designs for reference turbidimeters, and (2) by evaluating a variety of samples.

To avoid potential bias associated with a single method of comparison, the verification test used two reference methods for data comparisons: ISO 7027, “Water Quality—Determination of Turbidity”⁽¹⁾ and EPA Method 180.1, “Determination of Turbidity by Nephelometry.”⁽³⁾ Both of these methods measure turbidity using a nephelometric turbidimeter, but they differ in the type of light source and the wavelength used. ISO 7027 calls for an infrared light source, whereas Method 180.1 calls for a visible light source. The Monitek TST-SC is designed to conform to the requirements of ISO 7027, and thus that method is the appropriate reference for verification of the TST-SC performance. Verification results presented in this report, and summarized in the Verification Statement, are based on comparisons with the ISO 7027 data. However, secondary comparisons also are shown in this report, based on data from the TST-SC and Method 180.1. The secondary comparisons are of interest because Method 180.1 is widely recognized in the U.S. and is designated as the required method for drinking water compliance measurements. The secondary comparisons are shown only to illustrate the performance capabilities of the TST-SC and should not be taken as having equal weight as the comparisons with ISO 7027.

Additionally, to assess the response of the Monitek TST-SC turbidimeter to both prepared solutions and real-world water samples, verification involved both off-line and on-line phases. The off-line phase challenged the turbidimeter with a series of prepared standards and other test solutions to verify performance under controlled conditions. The on-line phase assessed long-term performance under realistic operating conditions by monitoring a sample stream in a municipal water treatment plant under normal operation. With the cooperation of the City of Columbus Water Division, both off-line and on-line phases were performed at the Dublin Road Water Plant in Columbus, Ohio.

3.3 Experimental Apparatus

On-line turbidimeters measure turbidity continuously on flowing sample streams as opposed to the static grab samples analyzed by the bench-top reference turbidimeters. Consequently, great care was taken to ensure that the samples collected for reference analysis were representative of the sample flow measured by the Monitek TST-SC turbidimeter. A cylindrical distribution manifold provided identical sample streams to sample ports spaced equally around the circumference of the manifold. Throughout the verification test, three ports were used for the turbidimeters being verified, and one port provided a stream for the grab samples. A single port centered in the bottom of the manifold introduced the sample stream to the distribution manifold. All the ports were tapped for ½" male normal pipe thread (NPT) fittings, and hard plastic compression fittings were used to connect the distribution manifold to the tubing (½" OD polyethylene) used in the recirculation system. Using a consistent tubing size and fitting style enabled rapid switching of the turbidimeters on a scheduled basis among the ports on the distribution manifold. Providing identical samples to each of the manifold ports minimized biases arising from water quality or turbulence issues; rotation of the technologies to each of these ports was used to identify if biases existed.

A schematic representation of this recirculation system is provided in Figure 3-1, where T1 through T3 represent the three on-line turbidimeters undergoing verification testing. T1 represents the Monitek TST-SC turbidimeter. Prepared solutions were supplied to all three turbidimeters simultaneously in a closed-loop recirculation system that used a 40-L reservoir and a centrifugal pump. Stream water from the plant was sampled from a pressurized source in a once-through configuration (i.e., without use of the pump or reservoir). In-line particle filters were inserted into the water flow using appropriate valving when reduction of turbidity levels was needed.

Before verification testing began, a series of five grab samples was collected from each port on the cylindrical manifold while recirculating a formazin solution with a nominal turbidity of 0.5 nephelometric turbidity unit (NTU). These samples were analyzed with the reference turbidimeters and compared to ensure uniformity of the turbidity of the solution. Comparison of the sample analyses indicated agreement in turbidity readings within $\pm 5\%$ among all of the ports.

Before verification testing began, the on-line turbidimeters verified in this test were installed in the test apparatus at the Dublin Road Water Plant. The Monitek TST-SC turbidimeter (Serial Number 0618) was installed by Battelle and inspected by a field representative of Monitek. As supplied, the Monitek turbidimeter included 1-1/2" female NPT fittings for direct in-line pipe mounting. Reducing fittings were used to couple the turbidimeter to the recirculation system, which was built with 1/2" OD tubing and 1/2" NPT plastic compression fittings. Much of the recirculation system, including the flow meters and the distribution manifold, was mounted to a 1/4"-thick aluminum panel installed in the water plant specifically for this verification test. The TST-SC turbidimeter was bolted to the panel using two L brackets that sandwiched the turbidimeter housing and were held in place using two of the six bolts around the housing circumference. Since the diameter of the tubing was smaller than the inside diameter of the Monitek TST-SC turbidimeter, the system was mounted vertically to ensure that no pockets of air were present in the turbidimeter during testing.

No control unit was provided with the Monitek TST-SC turbidimeter for verification testing, although control units are available from Monitek. Power was supplied to the sensor using a Lambda LQ-415 power supply (0 to 250 V, 80 mA, Battelle Asset Number LN 426441) provided by Battelle. The Monitek turbidimeter sensor was provided with 9 to 10V power from this power supply throughout the verification test. The sensor output was converted from a 4 to 20 mA signal to a direct current (DC) voltage using a precision resistor, and was recorded every 10 seconds throughout the test using LabTech Notebook software, which was run on a personal computer at the test site.

3.4 Reference Instruments

Owing to the nature of turbidity measurement and the inherent differences in response arising from different instrumental designs, separate bench-top turbidimeters meeting the design criteria detailed in ISO 7027⁽¹⁾ and EPA Method 180.1⁽³⁾ were used as reference instruments in this test. Both methods describe procedures to measure the nephelometric light scattering of a formazin solution, albeit with different prescribed instrumental design parameters. The primary difference

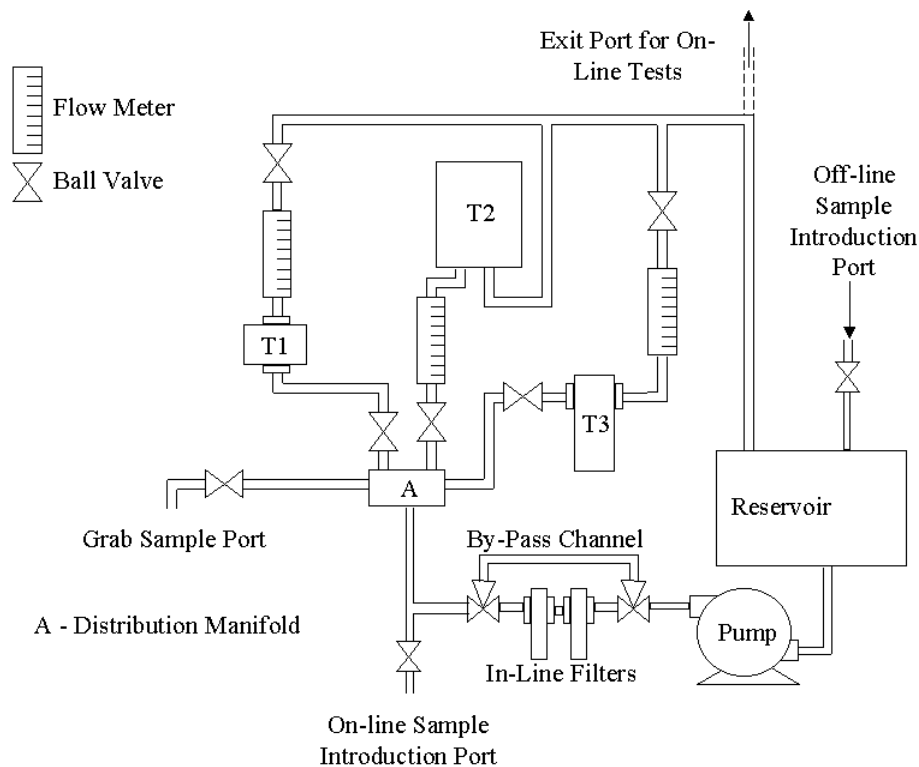


Figure 3-1. Schematic Representation of Recirculation System

between these two methods is in the choice of light source. Method 180.1 requires the use of a broadband incandescent tungsten lamp, while ISO 7027 requires the use of a narrowband IR source. Since the TST-SC is designed to comply with ISO 7027 requirements, that reference method is the basis for this verification. Comparisons of data with Method 180.1 are also shown, however, because of the widespread recognition and use of that method. Method 180.1 comparisons are secondary to the ISO 7027 comparisons used for verification. The bench-top turbidimeters used as the reference methods were the Hach 2100AN (Serial Number 980300001366) and the Hach 2100AN IS (Serial Number 950700000173), which, according to the manufacturer's literature, comply with the design specifications described in ISO 7027⁽¹⁾ and EPA Method 180.1⁽³⁾, respectively. Throughout the test the reference turbidimeters were operated in the non-ratio mode.

3.5 Off-Line Testing

The off-line phase of the verification test involved off-line sample introduction aimed at assessing the linearity, accuracy, and precision of the Monitek TST-SC on-line turbidimeter relative to the reference methods. Additionally, response to various upset conditions was quantified. As a means of testing these parameters, the off-line test phase included the introduction of standard formazin solutions or other samples, and the intentional manipulation of flow and water quality parameters.

Throughout the verification test, continuous turbidity measurements from the Monitek turbidimeter were recorded at preset intervals using LabTech Notebook software. Grab samples were collected simultaneously with some of these recorded measurements and analyzed using bench-top reference turbidimeters to provide a basis of comparison for the performance evaluations. The collection of grab samples was timed to coincide within 10 seconds with the recording of real-time turbidity measurements from the Monitek TST-SC, and the grab samples were analyzed within three minutes after collection to minimize possible temperature and settling effects.

Additionally, off-line testing included monitoring the instrumental responses of the Monitek turbidimeter to variations in water temperature, flow rate, and color. Each of these parameters was varied within a range consistent with conditions encountered under typical plant operation. The following subsections describe the procedures used for the off-line phase of the verification test.

Table 3-2 provides a summary of the parameters tested in the off-line phase, the test solutions used, and the number of readings recorded for each parameter.

Table 3-2. Summary of Measurements for Off-Line Testing

| Parameter Tested | Test Solution | Number of Readings |
|--|----------------------------|-------------------------|
| Linearity | Filtered water (< 0.1 NTU) | 5 |
| Linearity (accuracy, precision) ^a | 0.3 NTU Formazin | 5 |
| Linearity (accuracy, precision) | 0.5 NTU Formazin | 5 |
| Linearity (accuracy, precision) | 2 NTU Formazin | 5 |
| Linearity (accuracy, precision) | 5 NTU Formazin | 5 |
| Water Temperature Effect | 0.3 NTU Formazin | 5 each at 16, 21, 27°C |
| Water Temperature Effect | 5 NTU Formazin | 5 each at 16, 21, 27°C |
| Flow Rate Effect | 0.3 NTU Formazin | 5 |
| Flow Rate Effect | 5 NTU Formazin | 5 |
| Color Effect | ~ 0.1 NTU | 5 each at 5, 15, 30 CU |
| Color Effect | 5 NTU Formazin | 5 each at 35, 45, 60 CU |

a: () indicates additional parameters analyzed using collected data.

3.5.1 Linearity

Linearity was measured in the range from approximately 0.05 to 5 NTU as an initial check in the off-line phase. The recirculation system was filled with distilled, dionized water, which was then recirculated and filtered in the test apparatus using a 0.2- μm pleated polypropylene filter for 24 hours. After filtering, the in-line filter was bypassed and the turbidity of the water in the recirculation system was measured to be approximately 0.05 NTU. A series of five turbidity measurements was taken at that turbidity level with intervals of at least five minutes between successive measurements. A corresponding set of five measurements also was recorded at approximately 0.3, 0.5, 2, and 5 NTU. To reach each turbidity level, a small amount of 4000 NTU StablCal formazin stock solution was diluted in the recirculation system and allowed to flow through the recirculation system unfiltered for at least 15 minutes before turbidity readings were recorded. At each turbidity level, a series of five turbidity readings was recorded with at least a 5-minute interval between successive readings. These readings were compared to the reference measurements of grab samples collected simultaneously with each reading; that is, the turbidity of the solutions was determined by measurement with the reference turbidimeters, rather than simply by calculations based on the dilution process. After the prescribed measurements were recorded at each turbidity level, additional formazin stock solution was added to the recirculation system to increase the turbidity of the solution to the next value in the series.

Before measurements were recorded, the calibration of the reference turbidimeters was checked using a 0.5 NTU StablCal formazin solution purchased from Hach Company, Loveland, Colorado. Pursuant to the requirements of the test/QA plan,⁽¹⁾ agreement between the reference measurement and the certified turbidity of the standard was required to be within 10% before recording any series of measurements. After each series of measurements, the calibration of the reference turbidimeters was again checked with the same standard, and the same acceptance limits were applied. In addition to the 0.5 NTU calibration checks, before and after the measurements on the filtered water, a < 0.1 NTU blank standard also was measured to ensure proper calibration of the reference instruments at low levels. The < 0.1 NTU standard also was purchased from Hach Company; agreement between the reference measurement and the turbidity reported on the certificate of analysis was required to be within 0.02 NTU.

3.5.2 Accuracy and Precision

Data obtained from the linearity measurements were used to establish the accuracy and precision of the Monitek turbidimeter measuring formazin solutions. Accuracy was assessed by comparing continuous turbidity measurements with those from the ISO 7027 reference turbidimeter. Precision was assessed from the five replicate results at each turbidity level.

3.5.3 Water Temperature

Variations in the temperature of the water stream were introduced to simulate a range of conditions under which the on-line turbidimeters may typically operate. During off-line testing, the temperature of the recirculating water equilibrated in the range from 27 to 29°C, which was

approximately 3 to 6°C above the room temperature at the water plant during testing. To assess the effect of temperature on the turbidimeter performance, the temperature of the recirculating solution was lowered using an immersion type chiller, and replicate turbidity measurements were recorded at approximately 21°C and again at 16°C. In these tests, the solution temperature in the reservoir was held within 2.5 degrees of the nominal 16°C and 21°C targets, while a series of five measurements was recorded at each temperature. To ensure equilibration, the solution was allowed to recirculate for one hour before the turbidity measurements were recorded. For the temperature tests at 16°C and 21°C, the temperature of the sample stream was recorded at the grab sample port within 30 seconds of sample collection, and the temperature of the grab sample was measured within 30 seconds of completion of the reference measurement. To assess temperature effects at different turbidities, this test was conducted with both 0.3 and 5 NTU solutions.

3.5.4 Flow Rate

The flow rate of the sample stream through the Monitek TST-SC turbidimeter was manipulated to assess the response of the turbidimeter to various realistic operational conditions. Manual valves, which were included upstream and downstream of the Monitek turbidimeter, were adjusted to vary the flow rate through the turbidimeter while maintaining a back pressure on the line. During normal testing, the flow rate was held in the range from 0.2 to 0.5 gallons per minute (gpm). In contrast, the flow test was performed at a minimum flow rate of 0.1 gpm and at a maximum flow rate of 1.0 gpm. To assess the effect of flow rate on performance, measurements were made at both the minimum and maximum flow rates at turbidity levels of both 0.3 NTU and 5 NTU.

3.5.5 Color

Changes in water color were introduced by spiking the sample stream with colored solutions prepared from commercial food coloring dye. Stock solution was added to the system reservoir to give sample solutions approximately 5, 15, and 30 color units (CU) successively, and the instrumental response to these color changes was monitored. Five measurements were made for each color level at both low turbidity (~ 0.1 NTU) and higher turbidity (~ 5 NTU).

The color of the recirculated solution was determined by analyzing the grab samples instrumentally using the Hach 2100AN reference turbidimeter with the supplied light filter. This reference turbidimeter was calibrated for color measurements according to the instrument manual. Solutions used in the color calibration of the reference turbidimeter were prepared by dilution of a commercial cobalt-platinum color standard⁽⁴⁾ (Hach Company, Loveland, Colorado).

At ~ 0.1 NTU, the color of the solution before the addition of the dye was approximately 0 color unit (CU). However, at the 5 NTU level, light scattering from the presence of formazin introduced an apparent color to the solution of approximately 30 CU. Consequently, for the 0.5 NTU test, dye solution was added to increase the color by 5, 15, and 30 CU; i.e., to bring the absolute color to approximately 35, 45, and 60 CU, respectively.

3.6 On-Line Testing

The on-line test phase focused on assessing the long-term performance of the Monitek turbidimeter under realistic unattended operating conditions and assessing its accuracy in monitoring an actual sample stream. Specifically, this phase of testing addressed the calibration and drift characteristics of the turbidimeter over a five-week period of monitoring a sample stream from the water plant. Routine reference measurements were used for comparison with the on-line readings to assess accuracy, and a re-evaluation of the calibration at the end of the test period helped establish drift characteristics. Natural meteorological and demand changes contributed to the variability of water quality in the treatment facility and provided a natural range of turbidity for characterizing performance.

Table 3-3 provides a summary of the parameters tested in the on-line phase, the test solutions used, and the number of readings recorded for each parameter.

3.6.1 Accuracy

In the on-line testing, the accuracy of the Monitek TST-SC turbidimeter relative to the ISO 7027 reference method was assessed on water samples from the plant stream. A sample stream was drawn from a flocculation settling basin at the Dublin Road Water Plant facility, containing unfiltered water that had been treated with lime, caustic, and alum. The sample stream was directed to the Monitek TST-SC turbidimeter through the distribution manifold. Two grab samples of this stream were collected and analyzed by the reference turbidimeters each weekday (Monday through Friday) for the four weeks of testing. The reference measurements of these samples were compared with the simultaneous results from the Monitek TST-SC turbidimeter.

Table 3-3. Summary of Measurements for On-Line Testing

| Parameter Tested | Test Solution | Number of Readings |
|------------------|------------------|--|
| Accuracy | Plant Water | 2 per weekday for 4 weeks (40 total) |
| Drift | 0.3 NTU Standard | 5 for final linearity check |
| Drift | 0.5 NTU Standard | 5 each for eight calibration checks and 5 for final linearity check |
| Drift | 2 NTU Standard | 5 for final linearity check |
| Drift | 5 NTU Standard | 5 for final linearity check |

3.6.2 Drift

Drift was determined in two ways: (1) through off-line calibration checks conducted regularly throughout the course of the verification test using formazin solutions and (2) through a

comparison of multi-point linearity checks performed initially during the off-line phase described in Section 3.5.1 and subsequently after the completion of the on-line phase. The Monitek TST-SC turbidimeter was calibrated by the vendor prior to shipment and installation at the water plant. **After that calibration, no further manual calibration or adjustment was performed for the duration of the verification test period.** However, during the course of the on-line testing the Monitek TST-SC turbidimeter was observed to drift toward higher turbidity relative to the reference measurements on several occasions. When this behavior was observed, the Monitek TST-SC turbidimeter was taken off line briefly for cleaning, and the cylindrical window was cleaned with lint-free laboratory towels.

The Monitek TST-SC turbidimeter was taken off line briefly twice each week for routine calibration checks against a 0.5 NTU formazin solution. These intermediate calibration checks were performed twice weekly for four consecutive weeks. Freshly prepared 0.5 NTU formazin solutions were used for the standard solution.

Upon completion of the four-week period, calibration and linearity were checked again by comparison with the reference measurements using standard solutions of 0.3, 0.5, 2, and 5 NTU. A linear fit of these data was compared with the initial linearity check performed in the off-line phase to assess the degree of calibration drift.

Chapter 4

Quality Assurance/Quality Control

Quality control (QC) procedures were performed in accordance with the quality management plan (QMP) for the AMS pilot⁽⁵⁾ and the test/QA plan⁽²⁾ for this verification test.

4.1 Data Review and Validation

Test data were reviewed and approved according to the AMS pilot QMP,⁽⁵⁾ the test/QA plan,⁽²⁾ and Battelle's one-over-one policy. The Verification Test Coordinator, or the Verification Test Leader, reviewed the raw data and the data sheets that were generated each day and approved them by adding their signature and the date. Laboratory record notebook entries were also reviewed, signed, and dated.

4.2 Deviations from the Test/QA Plan

During the preparation and performance of the verification test, deviations from the test/QA plan were implemented to better accommodate differences in vendor equipment and other changes or improvements. Any deviation required the approval signature of Battelle's Verification Testing Leader. A planned deviation form was used for documentation and approval of the following changes:

1. Commercial food coloring dye was used for the color test instead of diluted color standard owing to the strongly acidic nature of the cobalt-platinum standard solution.
2. Calibration of the pH meter was performed only once during the test, and the meter was not readjusted to account for variations in ambient temperature. Recalibration was to be performed under the conditions of the test. However, the pH measurements were used only to assess changes and not for absolute measurements.
3. Only one in-line filter was used in the recirculation system.
4. The schedule of tests was lengthened and the order of testing was changed to better group series of parameter evaluations and to respond to unexpected experimental results.

These deviations had no significant impact on the test results used to verify the performance of the on-line turbidimeters.

4.3 Calibration

4.3.1 Reference Turbidimeters

The reference turbidimeters were calibrated according to the procedures described in their respective instrument manuals. The calibrations were performed on August 23, 1999. Calibration was performed using a blank, and 20, 200, 2000, and 7500 NTU StablCal calibration standards (Hach Company, Loveland, Colorado). After calibration and before proceeding with the verification test, the calibration of each reference turbidimeter also was checked through a five-point linearity test using solutions with the following turbidities: < 0.1, 0.3, 0.5, 2, and 5 NTU. The < 0.1, 0.3, and 0.5 NTU solutions were purchased and used as is, whereas the 2 and 5 NTU solutions were prepared by diluting a purchased 20 NTU StablCal formazin standard solution. The results of the linearity check are summarized in Table 4-1, indicating that the two reference turbidimeters gave essentially identical results. For each reference turbidimeter, the slope of this linear fit was within the 0.90 and 1.10 limits prescribed in the test/QA plan,⁽¹⁾ and each fit had an $r^2 > 0.98$ as called for in the test/QA plan.⁽¹⁾

Table 4-1. Results of Linearity Check of Reference Turbidimeters

| Parameter | Hach 2100AN IS (ISO 7027) | Hach 2100AN (180.1) |
|-----------------|---------------------------|---------------------|
| Slope | 1.086 | 1.086 |
| Intercept (NTU) | 0.004 | 0.010 |
| r^2 | 0.9991 | 0.9996 |

The calibration of each reference turbidimeter also was checked both before and after each series of test measurements, using a nominal 0.5 NTU StablCal standard solution. The reference turbidimeters were to be recalibrated if agreement between the turbidity reading and the certified 0.521 NTU turbidity value of this standard solution was not within $\pm 10\%$ (i.e., 0.469 to 0.573 NTU). If this calibration check criterion was met before, but not after, a series of test measurements were performed, those measurements were to be repeated after recalibration of the reference turbidimeters. Throughout the course of the verification test, neither reference turbidimeter was ever found to be out of calibration, and consequently no recalibration of the reference turbidimeters was performed.

Before the background readings were measured for the detection limit determination, an additional calibration check with < 0.1 NTU standard was also performed on the reference turbidimeters to ensure proper calibration at low levels. These calibration checks were performed on September 9, 1999, for the initial linearity test and October 20, 1999 for the final linearity test. The results showed agreement within 0.02 NTU between the turbidity reading of the < 0.1 NTU standard, and the value as reported on the certificate of analysis.

4.3.2 Temperature Sensors

A Fluke 52 thermocouple (Battelle Asset Number 570080) was used throughout the verification test to determine water temperature and the ambient room temperature. This thermocouple was calibrated on June 30, 1999, against a calibrated temperature standard (Fluke 5500A, Battelle Asset Number SN-714755).

4.3.3 Flow Meters

The flow meter used in the verification test to measure the water flow through the Monitek TST-SC turbidimeter was a panel-mounted, direct-reading meter purchased from Cole-Parmer (Catalog Number P-03248-56), capable of measuring up to 1 gpm. The flow meter was factory calibrated, and was checked once during the verification test by measuring the time required to fill a container of known volume through the meter at settings of 0.2 gpm and 1.0 gpm. Table 4-2 summarizes the results of the flow rate checks.

Table 4-2. Summary of Flow Meter Calibration Check

| Flow Meter Setting (gpm) | Volume (gallon) | Time (seconds) | Calculated Rate (gpm) |
|-------------------------------------|----------------------------|---------------------------|----------------------------------|
| 0.2 | 2 | 590 | 0.20 |
| 1.0 | 1 | 55 | 1.09 |
| 1.0 | 2 | 115 | 1.04 |
| 1.0 | 3 | 178 | 1.01 |

The calibration check was performed on August 26, 1999, and indicated agreement within the 10% criterion established in the test/QA plan⁽²⁾ at both the minimum and maximum flow rates.

4.3.4 pH Meter

The pH meter was calibrated once during the verification test, with no further adjustment of the meter. Calibration included standardization at a pH of 7 and a pH of 10 using buffer solutions. Calibration checks performed during the color test indicated a bias of 0.1 to 0.3 pH units. Biases above 0.2 pH units fall outside of the acceptance criterion for the verification test and introduce an uncertainty to the absolute magnitude of the pH readings. However, the pH readings were recorded as a means of assessing if changes in the acidity of the solution occurred as a result of adding the color solution, rather than as an absolute measure of the pH itself. The pH readings recorded during the test indicated no evidence of pH change in the test solution as the result of adding dye to the test solution.

4.4 Data Collection

Electronic data were collected and stored by a PC-based data acquisition system using LabTech Notebook software (Version 8.0.1). Data were collected from the Monitek TST-SC turbidimeter every 10 seconds over much of the course of verification testing. These data were saved in ASCII files along with the time of collection. Data files were stored electronically both on the hard drive of the data collection system and on floppy discs for backup purposes. Data collected manually included turbidity readings of the reference turbidimeters, flow rates, and water and ambient air temperature measurements. An example of the data recording sheet used to record these data is shown in Appendix A.

4.5 Assessments and Audits

4.5.1 Technical Systems Audit

Battelle's Quality Manager performed a technical systems audit once during the verification test. The purpose of this audit was to ensure that the verification test was performed in accordance with the test/QA plan⁽²⁾ and that all QA/QC procedures were implemented. In this audit, the Quality Manager reviewed the calibration standards and reference methods used, compared actual test procedures with those specified in the test/QA plan, and reviewed data acquisition and handling procedures. A report on this audit is provided in Appendix B.

4.5.2 Performance Evaluation Audit

Performance evaluation audits were conducted to assess the quality of the measurements made in the verification test. These audits addressed only those measurements made by Battelle staff in conducting the verification test, i.e., the reference turbidimeter readings and temperature measurements. The audits were conducted by analyzing the standards or comparing them with references that were independent of those used in the verification test. Each audit was made at least once during the verification test.

The audit of the reference turbidimeters was performed by analyzing a reference solution that was independent of the formazin standards used for calibration of the reference turbidimeters during the verification test. The independent reference solution was an AMCO AEPA-1 0.500 NTU standard solution obtained from APS Analytical Standards, Redwood City, California. This audit was conducted once daily throughout the verification test and served as an independent verification of the calibration of the reference turbidimeters. Agreement between the National Institute of Standards and Technology (NIST) traceable turbidity value of the AMCO AEPA-1 solution and the turbidity readings from each reference turbidimeter was recorded and tracked graphically using a control chart. Furthermore, similar calibration assessments were performed daily using a purchased 0.521 NTU StablCal formazin standard (Hach Company, Loveland, Colorado), as described in Section 4.3.1. The results of these daily calibration assessments always showed agreement between the turbidity reading from each reference turbidimeter and the true turbidity within $\pm 10\%$ as required in the test/QA plan.⁽²⁾ The results of

the daily calibration assessments are shown in Figures 4-1a and 4-1b, for both the AMCO AEPA-1 standard and the formazin standard on the ISO 7027 and Method 180.1 reference turbidimeters, respectively. (The dashed lines in the upper parts of Figures 4-1a and 4-1b are at intervals of 0.05 NTU, but are for visual reference only and are not exactly the $\pm 10\%$ control limits of the calibration checks. The bottom portion of each figure shows the $\pm 10\%$ control limits.) Throughout the course of the verification test, readings of the AMCO AEPA-1 standard, as measured by the ISO 7027 turbidimeter, ranged from -1.2% to +6.2% relative to the certified turbidity value for that standard, and were on average $\sim 2.7\%$ higher. For the Method 180.1 turbidimeter, the range was -1.2% to +5.4% with an average reading which was 1.7% higher than the certified turbidity value. The daily fluctuations in these measurements resulted in standard deviations of $\sim 1.7\%$ for each reference turbidimeter. Similarly, readings of the formazin standard ranged from -5.2% to +8.4% for the ISO 7027 and from -6.9% to +8.3% for the Method 180.1. The average readings were higher than the certified turbidity value by $\sim 2.2\%$ when measured by the ISO 7027 turbidimeter and by $\sim 1.6\%$ for the Method 180.1 turbidimeter, with standard deviations of 3.5% and 3.7% respectively. Although the average deviations from the true turbidity values for these standards were approximately the same, the scatter in the readings was greater in the formazin readings.

The audit of the thermocouple used during the verification test consisted of a comparison of the temperature readings from the thermocouple with those of an independent temperature sensor. The thermocouple was checked for accuracy by comparison with an American Society for Testing and Materials mercury-in-glass thermometer in the Battelle Instrument Laboratory on October 13, 1999, and again on November 1, 1999. Those comparisons were done at ambient temperature, and the results are shown in Table 4-3.

Agreement between the thermocouple used in the verification test and the mercury-in-glass thermometer was well within the two-degree specification established in the test/QA plan.⁽²⁾

4.5.3 Verification Test Data Audit

Battelle's Quality Manager audited at least 10% of the verification data acquired during the verification test. The Quality Manager traced the data from initial acquisition, through reduction and statistical comparisons, and to final reporting. All calculations performed on the data undergoing the audit were checked.

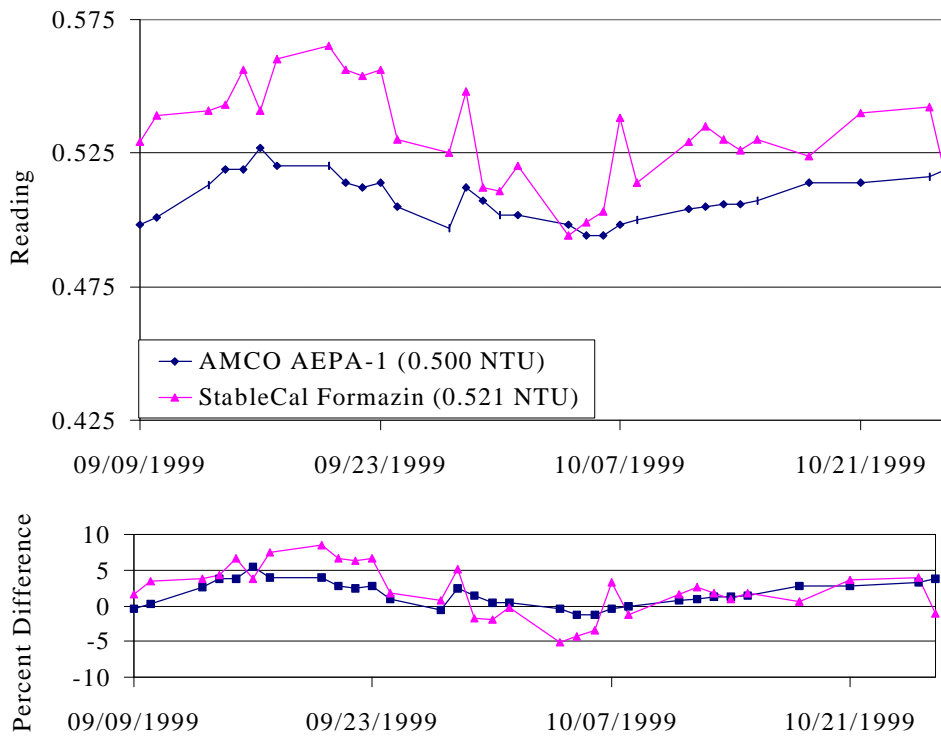


Figure 4-1a. Control Chart for Performance Evaluation Calibration Checks of the ISO 7027 Reference Turbidimeter

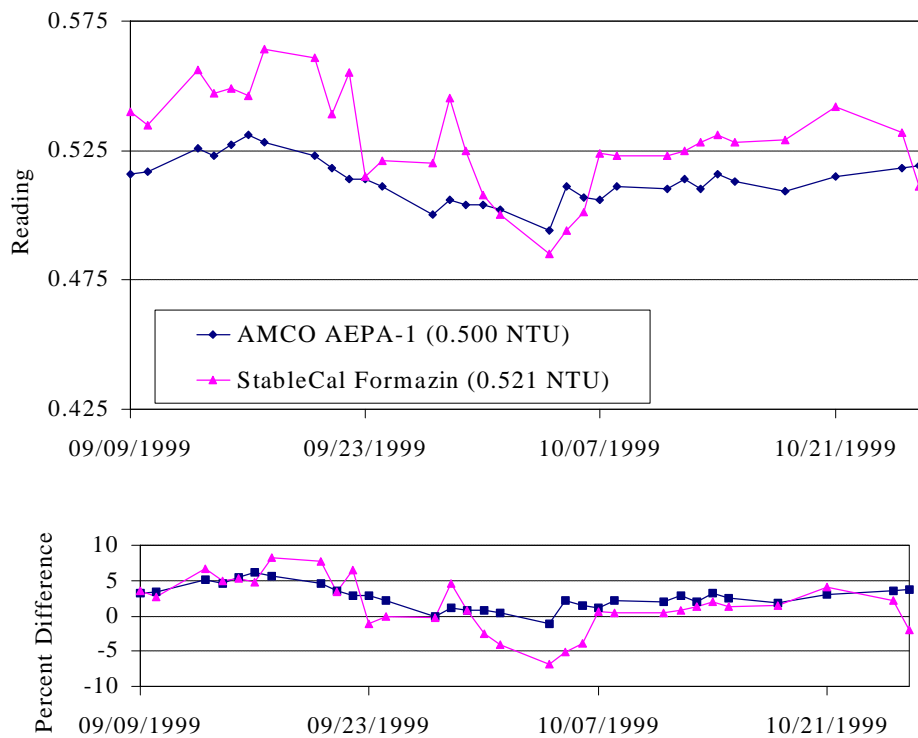


Figure 4-1b. Control Chart for Performance Evaluation Calibration Checks of the Method 180.1 Reference Turbidimeter

Table 4-3. Results of Calibration Checks of Thermocouple Used in Verification Test

| | October 13, 1999 | November 1, 1999 |
|-----------------------------------|------------------|------------------|
| Fluke 52 Thermocouple | 27.2°C | 29.5°C |
| ASTM Mercury-in-Glass Thermometer | 27.2°C | 29.7°C |

4.6 Audit Reporting

Each assessment and audit was documented in accordance with Section 2.9.7 of the Quality Management Plan for the AMS pilot.⁽⁵⁾ The assessment report included the following:

- Identification of any adverse findings or potential problems
- Response to adverse findings or potential problems
- Possible recommendations for resolving problems
- Citation of any noteworthy practices that may be of use to others
- Confirmation that corrective actions have been implemented and are effective.

A copy of the Technical Systems Audit Report is included in Appendix B of this report.

Chapter 5 Statistical Methods

5.1 Off-Line Testing

The turbidimeter performance characteristics were quantified on the basis of statistical comparisons of the test data. This process began by converting the files that resulted from the data acquisition process into spreadsheet data files suitable for data analysis. The following statistical procedures were used to make the comparisons.

5.1.1 Linearity

Linearity was assessed by linear regression, with the reference turbidity reading (R) as an independent variable and the turbidimeter response (T) as a dependent variable. The regression model was

$$T = m_1 \times R + b$$

where μ_1 and β are the slope and intercept of the response curve, respectively. The turbidimeter performance was assessed in terms of the slope, intercept, and the square of the correlation coefficient of the regression analysis.

5.1.2 Accuracy

The accuracy of the turbidimeter with respect to the reference method was assessed in terms of the average relative bias (B), as follows:

$$B = \left(\frac{\overline{(R - T)}}{R} \right) \times 100$$

where R is the turbidity reading of the reference turbidimeter, and T is the corresponding turbidity reading of the Monitek TST-SC turbidimeter.

Accuracy relative to the reference turbidimeter was assessed both for the prepared solutions and the samples from the plant water stream. The accuracy of the Monitek TST-SC turbidimeter was assessed relative to the ISO 7027 reference method for verification purposes and relative to the 180.1 reference method as an illustration of performance.

5.1.3 Precision

Precision was reported in terms of the percent relative standard deviation (RSD) of a group of similar measurements. For a set of turbidity measurements given by T_1, T_2, \dots, T_n , the standard deviation (S) of these measurements is

$$S = \left[\frac{1}{n-1} \sum_{k=1}^n (T_k - \bar{T})^2 \right]^{1/2}$$

where \bar{T} is the average of the turbidity readings. The RSD is calculated as follows:

$$\text{RSD} = \frac{S}{\bar{T}} \times 100$$

and is a measure of the dispersion of the measurement relative to the average value of the measurements. This approach was applied to the groups of replicate measurements on each test solution. In some cases, the turbidity of the prepared solution changed approximately linearly with time, due to loss of particles in the recirculation system. In those cases, a linear regression of the data was performed to assess the slope of the turbidity change as a function of time. This slope was used to adjust the individual turbidity readings to approximately the initial concentration. The precision was then calculated on the adjusted values as described above.

5.1.4 Water Temperature Effects

The effect of water temperature on the response of the Monitek TST-SC at 0.3 NTU and 5 NTU was assessed by trend analysis. The turbidity readings relative to the ISO 7027 reference turbidimeter were analyzed as a function of water temperature to identify trends in the relative turbidity at each of the two levels of turbidity. The calculations were performed using separate linear regression analyses for the data at each turbidity level. A similar calculation was done for illustrative purposes using the 180.1 reference data.

5.1.5 Flow Rate Sensitivity

Analysis of flow rate influence on turbidity readings was similar to that for water temperature effects. The turbidimeter response relative to the ISO 7027 reference turbidimeter was analyzed as a function of flow rate to assess trends in the response of the turbidimeter with changes in sample flow rate. The analyses were performed separately for the 0.3 NTU and 5 NTU data. A similar calculation was done for illustrative purposes using the 180.1 reference data.

5.1.6 Color Effects

The influence of color on turbidity was assessed through a linear regression analysis of the turbidity measured for each color relative to the ISO 7027 reference turbidimeter. Separate

analyses were performed for the measurements recorded at 0.1 NTU and those recorded at 5 NTU. A similar calculation was done for illustrative purposes using the 180.1 reference data.

5.2 On-Line Testing

5.2.1 Accuracy

As described in Section 5.1.2, accuracy in the on-line measurements was determined as a bias relative to the ISO 7027 reference turbidimeter. Daily reference measurements of the sample stream from the water plant were used to assess for accuracy. A similar calculation was done for illustrative purposes using the 180.1 reference data.

5.2.2 Drift

Drift was assessed in two ways. The drift in the calibration of the Monitek TST-SC turbidimeter was assessed by comparison of the regression analyses of the multi-point linearity tests performed at the beginning and end of the verification test. This comparison was used to establish any long-term drift in instrumental calibration during the verification test. Also, the reference and on-line turbidity results in monitoring the plant water stream were used to assess drift associated with the operation of the instrument (e.g., fouling of the optics). Trends in the intermediate calibration data toward a positive bias were used to identify when the turbidimeter needed cleaning.

Chapter 6 Test Results

The results of the verification test are presented in this section, based upon the statistical methods of comparison shown in Chapter 5. For all performance characteristics verified, two sets of results are shown. The primary verification results are based on comparisons with the ISO 7027 reference method; a secondary illustration of performance is based on comparisons with the EPA 180.1 reference method.

6.1 Off-Line Testing

Off-line testing was performed to assess the performance of the Monitek TST-SC turbidimeter when measuring known solutions under controlled conditions. The first of the off-line tests was performed to establish the linearity of the turbidimeter response in the range from < 0.1 to 5 NTU. Data from the linearity test also were used to assess the accuracy and precision of the TST-SC in this turbidity range. After the linearity test, the effects of sample temperature, sample flow rate, and sample color were evaluated. The results of each of these tests are described in this section.

6.1.1 Linearity

The verification data from the initial linearity test are shown in Figure 6-1a, relative to the ISO 7027 reference turbidimeter. A series of at least five data points was recorded at each of the five nominal turbidity levels (approximately < 0.05, 0.3, 0.5, 2, and 5 NTU). At the two highest NTU, a decrease in turbidity was observed in the readings of both the Monitek TST-SC turbidimeter and the reference turbidimeter. This decrease can be seen graphically as a spread in the data along the slope of the linearity plots. Between the first and fifth readings at 2 NTU, the decrease in turbidity represented approximately 4 to 5% of the initial turbidity as measured by the reference turbidimeter. This decrease in turbidity was likely the result of formazin being lost from the solution in the recirculation system. In an attempt to prevent the formazin loss, the solution was stirred magnetically. A second series of five measurements was recorded at the 2 NTU level after magnetic stirring of the formazin solution was introduced. After magnetic stirring was introduced, the decrease in turbidity was still observed, however, to a slightly lesser extent (approximately 2 to 4%).

The Monitek TST-SC does not respond to turbidity levels below approximately 0.1 NTU. Consequently, the linearity of the Monitek TST-SC was established between 0.3 and 5 NTU.

The data from the linearity test, excluding the low turbidity readings, were fit using a linear regression as described in Section 5.1.1, and the results of these fits are shown in Table 6-1. The secondary comparison with the Method 180.1 data is shown in Figure 6-1b, with the regression results also shown in Table 6-1.

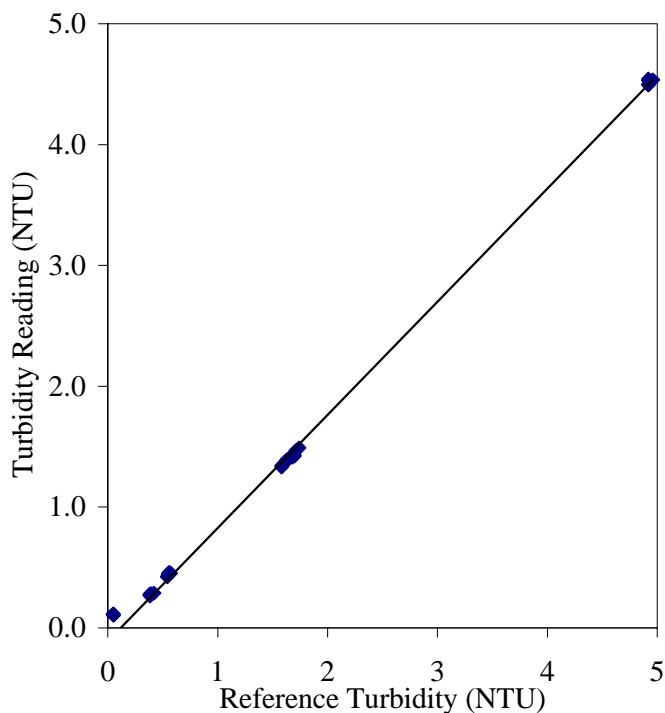


Figure 6-1a. Linearity Plot for Monitek TST-SC Turbidimeter vs. ISO 7027 Reference Turbidimeter

Table 6-1. Statistical Results of Initial Linearity Test on Monitek TST-SC Turbidimeter

| Linear Regression Parameter | Verification Results ^a | Secondary Comparison ^b |
|-----------------------------|-----------------------------------|-----------------------------------|
| Slope (std. error) | 0.935 (0.004) | 0.946 (0.005) |
| Intercept (std. error) NTU | -0.107 (0.010) | -0.089 (0.011) |
| r ² | 0.9996 (0.0331) | 0.9995 (0.0373) |

^a Comparison with ISO 7027 reference method (2100AN IS reference turbidimeter).

^b Comparison with EPA Method 180.1 (2100AN reference turbidimeter).

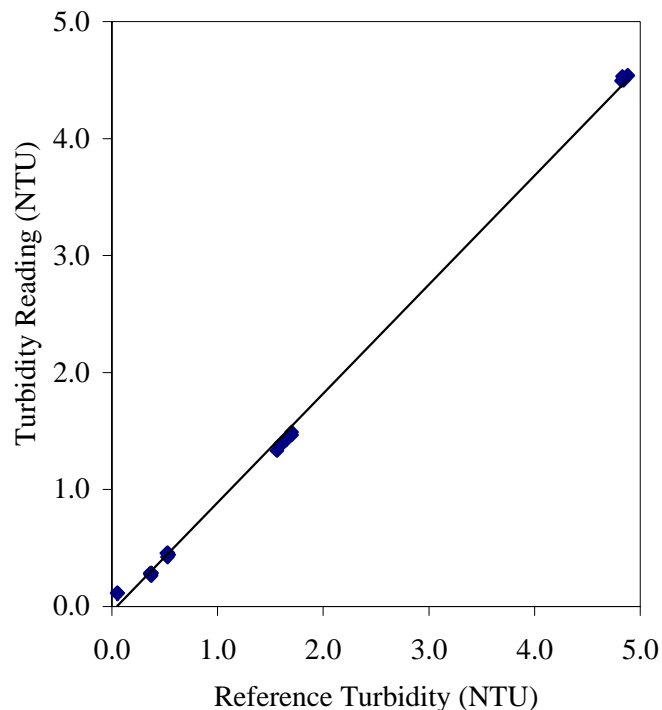


Figure 6-1b. Linearity Plot for Monitek TST-SC Turbidimeter vs. Method 180.1 Reference Turbidimeter

The verification results of the linear regression indicate that the Monitek TST-SC turbidimeter responded linearly to turbidity between 0.3 NTU and 5 NTU. The slope of the response curve was ~6.5% lower than unity with respect to the ISO 7027 reference turbidimeter, representing a negative bias in turbidity readings. A negative intercept (~ 0.1 NTU) was determined for the linearity plot, indicating an offset in the calibration curve of the Monitek TST-SC turbidimeter.

The secondary comparison in Table 6-1 shows that the TST-SC also exhibited good linearity relative to Method 180.1, with a similar slope and negative intercept of the response curve.

6.1.2 Accuracy

Data obtained from the initial linearity test were used to assess accuracy for the off-line tests. The results of the accuracy verification are given in Table 6-2 and are presented as the average difference between the Monitek TST-SC turbidimeter and each reference turbidimeter, as well as the relative bias of the Monitek TST-SC turbidimeter with respect to the reference measurements. Negative values indicate a negative bias in the Monitek TST-SC turbidimeter readings when compared with the reference turbidimeter.

Table 6-2. Bias of Monitek TST-SC Turbidimeter Relative to the Reference Measurements on Prepared Test Solutions

| Nominal Turbidity of Test Solution (NTU) | Verification Results ^a | | Secondary Comparison ^b | |
|--|-----------------------------------|-------------------|-----------------------------------|-------------------|
| | Average Difference (NTU) | Relative Bias (%) | Average Difference (NTU) | Relative Bias (%) |
| 0.3 | -0.114 | -28.9 | -0.089 | -24.0 |
| 0.5 | -0.109 | -19.7 | -0.078 | -14.9 |
| 2 | -0.249 | -15.0 | -0.217 | -13.5 |
| 5 | -0.407 | -8.2 | -0.329 | -6.8 |

^a Comparison with ISO 7027 reference method (2100AN IS reference turbidimeter).

^b Comparison with EPA Method 180.1 (2100AN reference turbidimeter).

The verification results in Table 6-2 show a bias of approximately 30% at 0.3 NTU and approximately 10% at 5 NTU, resulting from average measured differences of ~ 0.1 to ~ 0.4 NTU. It is worth noting that although there is a considerable relative bias in the Monitek readings, a large portion of this bias can be attributed to the intercept calculated from the linearity plots (Table 6-1). At the 0.3 and the 0.5 NTU turbidity levels, the calculated intercepts account for essentially 100% of the relative bias. Likewise, the calculated intercepts account for approximately 25 to 50% of the relative bias at each of the two higher turbidity levels. A shift in the calibration curve to eliminate the offset would result in a dramatic reduction in the observed bias.

The secondary comparison in Table 6-2 shows similar performance relative to Method 180.1, with average bias results of 24% at 0.3 NTU and 6.8% at 5 NTU.

6.1.3 Precision

Data from the linearity test were used to calculate precision at 0.3, 0.5, 2, and 5 NTU. At both the 2 NTU and 5 NTU levels, a decrease in turbidity was observed as a function of time during the test procedure. To account for this variability in turbidity, the readings at these two levels were analyzed by linear regression against time and adjusted to approximately the initial turbidity value using correction factors based on the regression results. The adjusted values (T_i') were calculated using the following equation:

$$T_i' = T_i + c(t_i - t_0)$$

where T_i is the i^{th} turbidity reading, t_i is the time at which the i^{th} sample was collected, t_0 is the time of collection for the initial sample in the series, and c is the slope of the line determined from the linear regression results of turbidity versus time at 2 NTU or 5 NTU. The results of the adjustment calculations are given in Table 6-3 for the Monitek TST-SC turbidimeter. Similar

corrections were applied to the reference readings since the reference readings showed the same trend of decreasing turbidity with time.

Table 6-3. Adjusted Turbidity Readings for Precision Calculations of the Monitek TST-SC Turbidimeter

| Nominal Value (NTU) | Actual Reading (NTU) | Corrected Reading (NTU) | Nominal Value (NTU) | Actual Reading (NTU) | Corrected Reading (NTU) |
|---------------------|----------------------|-------------------------|---------------------|----------------------|-------------------------|
| 2 | 1.4917 | 1.4917 | 5 | 4.5374 | 4.5374 |
| 2 | 1.4673 | 1.4841 | 5 | 4.5435 | 4.5535 |
| 2 | 1.4429 | 1.4766 | 5 | 4.5007 | 4.5207 |
| 2 | 1.4246 | 1.4751 | 5 | 4.5312 | 4.5612 |
| 2 | 1.4124 | 1.4797 | 5 | 4.4946 | 4.5346 |
| 2 | 1.3940 | 1.4782 | | | |
| 2 | 1.3757 | 1.4767 | | | |
| 2 | 1.3757 | 1.4935 | | | |
| 2 | 1.3452 | 1.4798 | | | |
| 2 | 1.3330 | 1.4845 | | | |

The precision was calculated from the raw data at the 0.3 and 0.5 NTU levels, and from the corrected data at the 2 NTU and the 5 NTU levels. The results of these calculations are shown in Table 6-4. For comparison, the calculated precision values for the two reference turbidimeters are also included in that table.

The results of these calculations indicate that the Monitek TST-SC turbidimeter has approximately the same precision as the bench-top reference turbidimeter through the range of turbidity measured in this verification test. The precision of the Monitek measurements ranged from 3.3% RSD at 0.3 NTU to 0.35% RSD at 5 NTU.

Table 6-4. Precision of Monitek TST-SC Turbidimeter and of the Reference Turbidimeters

| Nominal Turbidity | Monitek TST-SC | | ISO 7027 | | Method 180.1 | |
|-------------------|----------------|---------|----------|---------|--------------|---------|
| | SD | RSD (%) | SD | RSD (%) | SD | RSD (%) |
| 0.3 NTU | 0.0093 | 3.3 | 0.0161 | 4.1 | 0.0051 | 1.4 |
| 0.5 NTU | 0.0140 | 3.2 | 0.0118 | 2.1 | 0.0095 | 1.8 |
| 2 NTU | 0.0064 | 0.43 | 0.0123 | 0.71 | 0.0108 | 0.64 |
| 5 NTU | 0.0160 | 0.35 | 0.0126 | 0.26 | 0.0088 | 0.18 |

6.1.4 Water Temperature Effects

The verification data obtained for the temperature test are shown in Figure 6-2a. As a result of gradual loss of formazin in the recirculation system during the temperature test, additional formazin solution was added between each set of temperature measurements to maintain turbidity levels at approximately 0.3 NTU and 5 NTU. Consequently, the absolute turbidity readings alone cannot be used as an indication of temperature effects. Therefore, the readings recorded for the Monitek TST-SC turbidimeter were normalized to the corresponding reference readings to get a relative measure of turbidity. These relative values (i.e., ratios of TST-SC to ISO 7027 data) are shown in Figure 6-2a and were analyzed by linear regression to assess the effect of water temperature on turbidity reading. The results of the regression analysis are given in Table 6-5.

These verification results indicate a small temperature effect at the lower turbidity (0.3 NTU), suggesting a slight decrease in relative turbidity readings with increased temperature, i.e., the results indicate a statistically significant change in observed turbidity relative to the reference turbidimeters as a function of temperature. This change represents a relative difference of approximately 0.4% per degree C relative to the ISO 7027 reference turbidimeter. At the higher turbidity (5 NTU), the 95% confidence interval of the regression slope includes zero, and thus the data indicate no statistically significant relation between turbidity readings and water temperature.

The secondary results in Figure 6-2b and Table 6-5 indicate a temperature effect resulting in a relative decrease in turbidity of 1.1% per degree C at 0.3 NTU. At the 95% confidence level, no statistically significant effect is observed at 5 NTU.

6.1.5 Flow Rate

The results of the flow rate test are summarized in Figure 6-3. The data are again presented and analyzed as relative turbidity readings, rather than absolute turbidity readings to correct for a gradual, slight loss of the formazin during the testing. The results of the statistical analysis of the flow data are presented in Table 6-6.

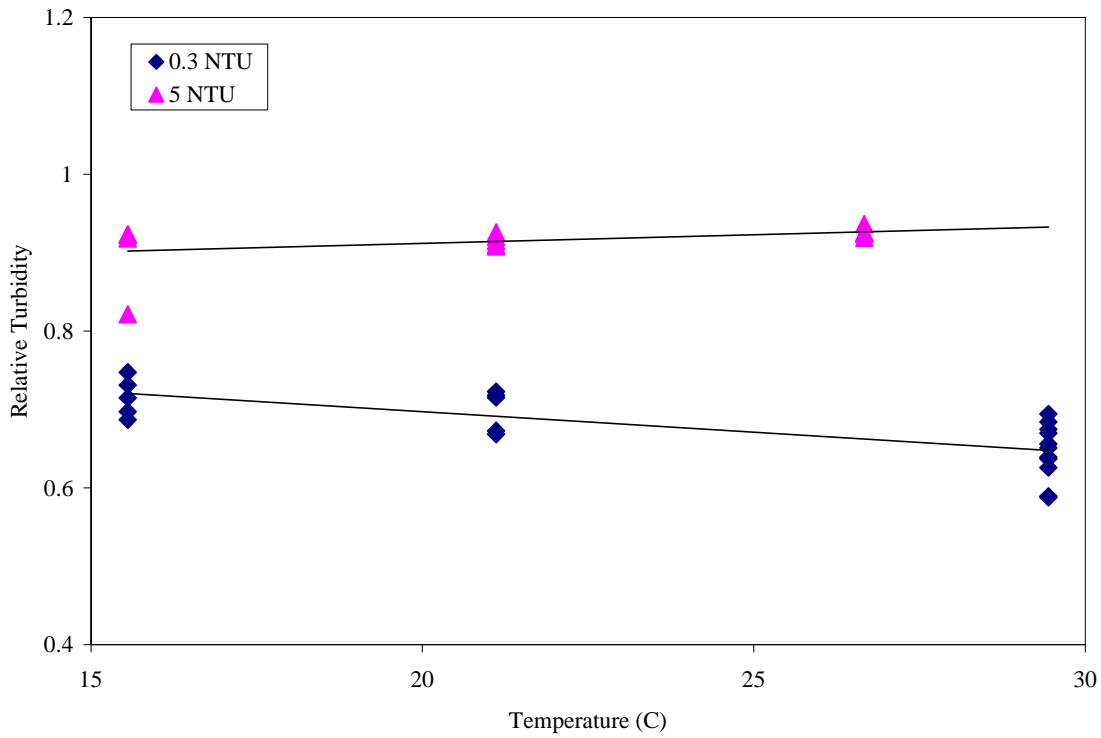


Figure 6-2a. Effect of Temperature on Monitek TST-SC Turbidity Readings vs. ISO 7027 at Both 0.3 and 5 NTU

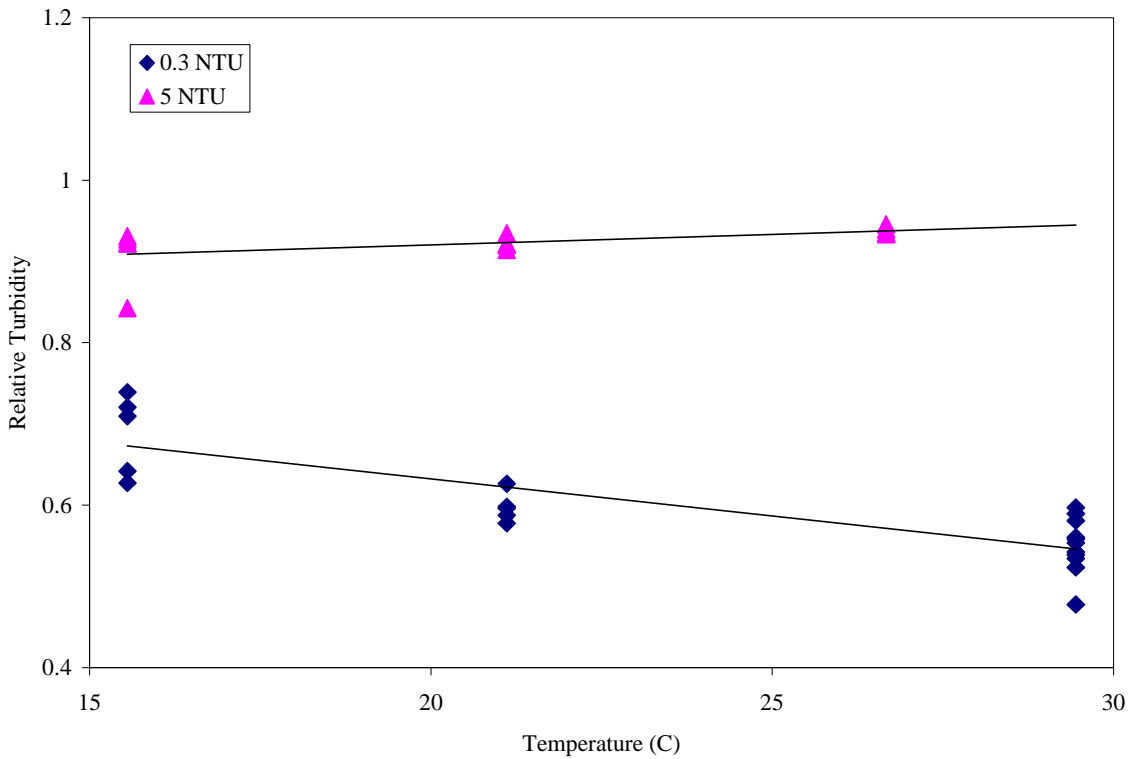


Figure 6-2b. Effect of Temperature on Monitek TST-SC Turbidity Readings vs. Method 180.1 at Both 0.3 and 5 NTU

Table 6-5. Statistical Results of Temperature Test on the Monitek TST-SC Turbidimeter

| Linear Regression Parameter | Verification Results ^a | | Secondary Comparison ^b | |
|--------------------------------|-----------------------------------|--------------------|-----------------------------------|--------------------|
| | 0.3 NTU | 5 NTU | 0.3 NTU | 5 NTU |
| Slope (std. error) | -0.0042 (0.0013) | 0.0022 (0.0014) | -0.0108 (0.0016) | 0.0026 (0.0012) |
| Intercept (std. error) | 0.784 (0.030) | 0.869 (0.031) | 0.844 (0.036) | 0.869 (0.026) |
| r ² (std. error) | 0.427 (0.030) | 0.150 (0.026) | 0.775 (0.036) | 0.257 (0.021) |

^a Comparison with ISO 7027 reference method (2100AN IS reference turbidimeter).

^b Comparison with EPA Method 180.1 (2100AN reference turbidimeter).

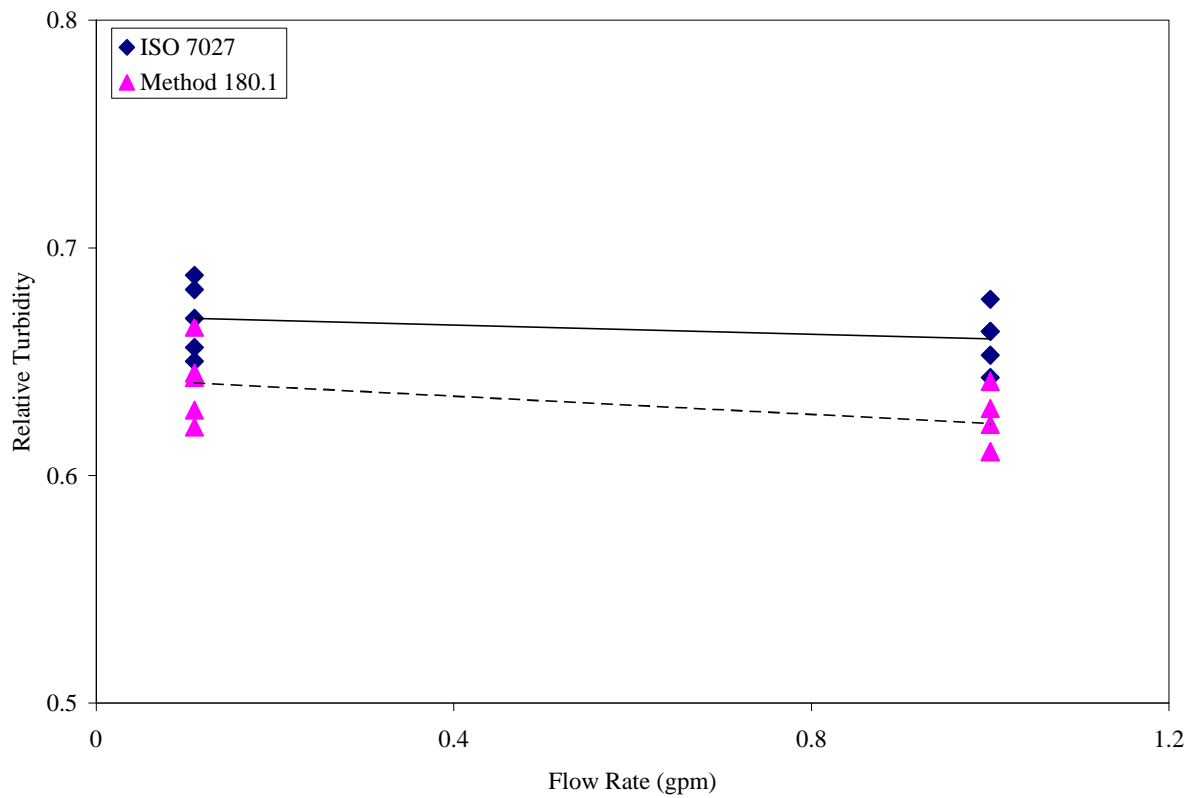


Figure 6-3. Effect of Sample Flow Rate on Monitek TST-SC Turbidimeter Response

Table 6-6. Statistical Results of Flow Rate Test for the Monitek TST-SC Turbidimeter

| Parameter | Verification Results^a | Secondary Comparison^b |
|-----------------------------|---|---|
| Slope (std. error) | -0.010 (0.010) | -0.020 (0.011) |
| Intercept (std. error) | 0.670 (0.007) | 0.643 (0.008) |
| r ² (std. error) | 0.0107 (0.015) | 0.303 (0.015) |

^a Comparison with ISO 7027 reference method (2100AN IS reference turbidimeter).

^b Comparison with EPA Method 180.1 (2100AN reference turbidimeter).

The 95% confidence intervals for the slopes both include zero, indicating that sample flow rate has no significant effect on the response of the Monitek TST-SC turbidimeter in the range of 0.1 to 1.0 gpm.

6.1.6 Color Effects

The verification data obtained from the color tests at 0.1 NTU and 5 NTU are shown in Figure 6-4a. In this figure, the data at each color level are plotted as relative values with respect to the reference turbidimeter readings, and the statistical analysis of these data involved a linear regression analysis of the relative data as a function of solution color. At the 5 NTU level, the background color reading of approximately 30 CU was subtracted, and only the effect of color added during the test is shown. The results of the statistical calculations are summarized in Table 6-7.

The verification results in Table 6-7 show that at the 5 NTU level, color has no significant effect (95% confidence) on the response of the Monitek TST-SC turbidimeter. At the low turbidity level, color has a small but statistically significant effect on the response of the Monitek TST-SC turbidimeter. However, that test was performed at a turbidity level of approximately 0.1 to 0.2 NTU, which is near the instrumental detection limit of the Monitek TST-SC turbidimeter. Consequently, it is unclear whether the observed effect is the result of an actual response to color, or if it is the result of measurements taken at the low end of the measuring range for the turbidimeter. Similar results are shown for the secondary comparison in Figure 6-4b and Table 6-7.

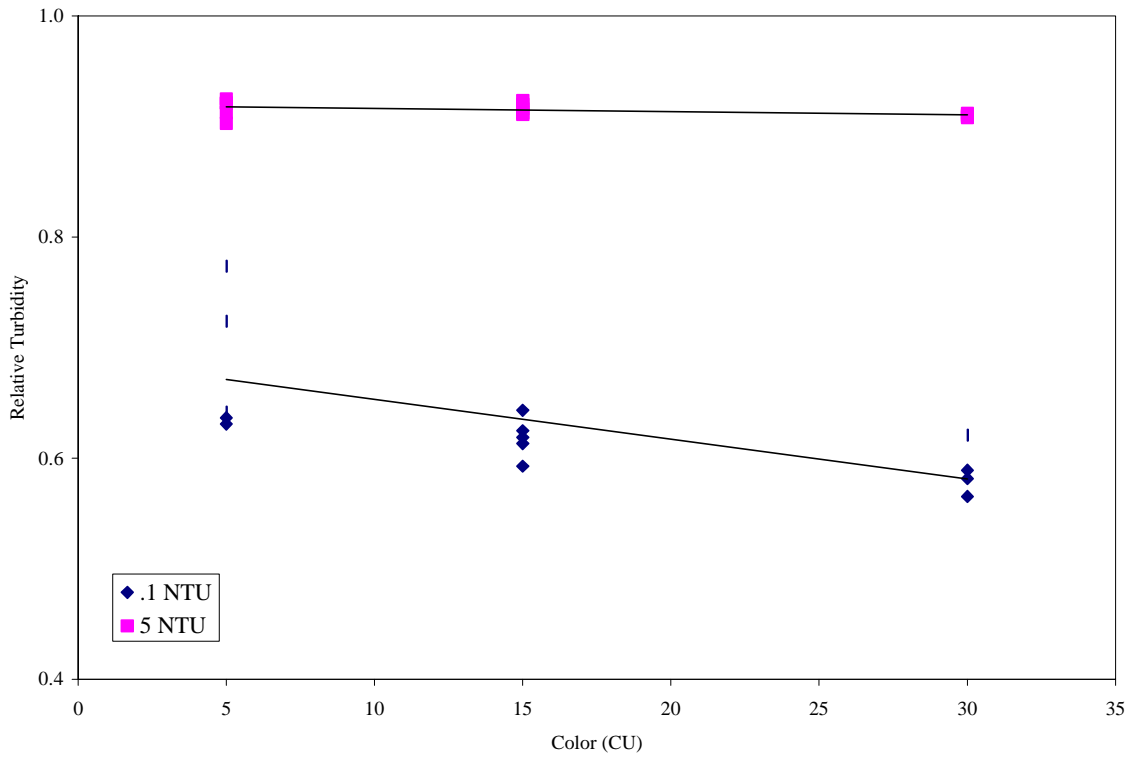


Figure 6-4a. Effect of Color on Relative Turbidity with the Monitek TST-SC Turbidimeter vs. the ISO 7027 at Both 0.1 and 5 NTU

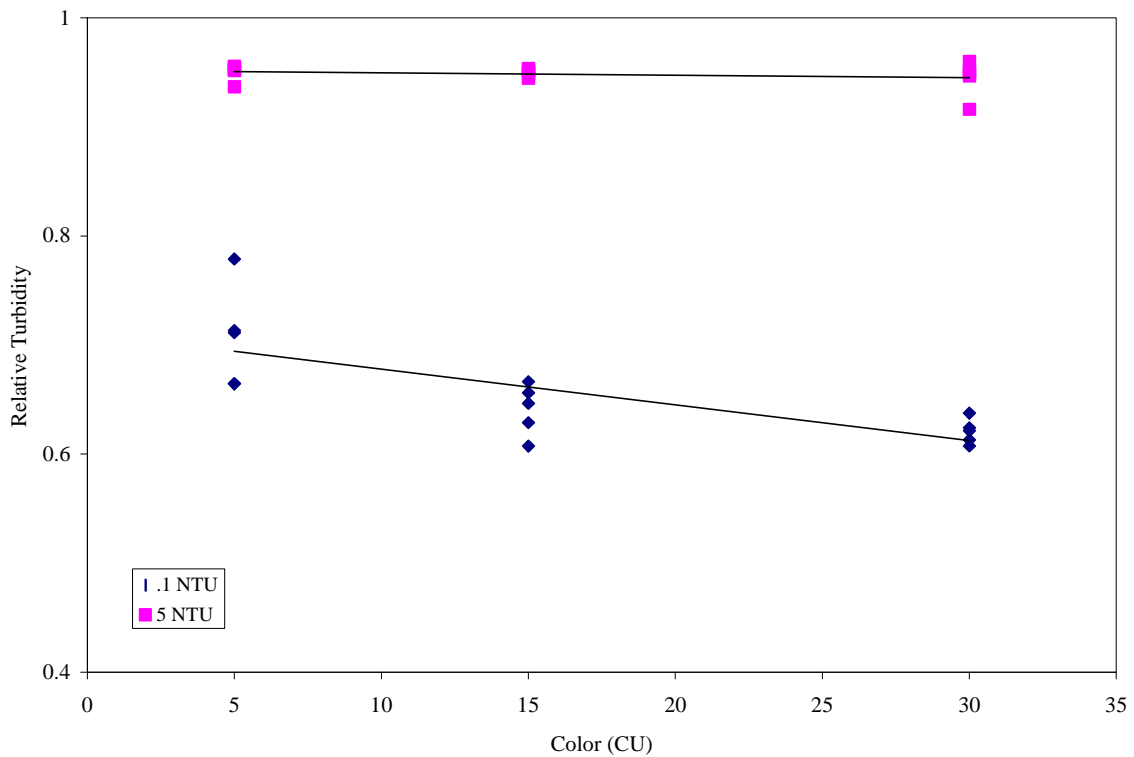


Figure 6-4b. Effect of Color on Relative Turbidity with the Monitek TST-SC Turbidimeter vs. Method 180.1 at Both 0.1 and 5 NTU

Table 6-7. Statistical Results of the Color Test with the Monitek TST-SC Turbidimeter

| Reference: Parameter | Verification Results ^a | | Secondary Comparison ^b | |
|--------------------------------|-----------------------------------|---------------------|-----------------------------------|---------------------|
| | 0.1 NTU | 5 NTU | 0.1 NTU | 5 NTU |
| Slope (std. error) | -0.0036 (0.0010) | -0.0003 (0.0001) | -0.0033 (0.0008) | -0.0002 (0.0003) |
| Intercept (std. error) | 0.6894 (0.0201) | 0.9192 (0.0029) | 0.7106 (0.0166) | 0.9521 (0.0051) |
| r ² (std. error) | 0.4871 (0.0408) | 0.2224 (0.0059) | 0.5340 (0.0337) | 0.0564 (0.0104) |

^a Comparison with ISO 7027 reference method (2100AN IS reference turbidimeter).

^b Comparison with EPA Method 180.1 (2100AN reference turbidimeter).

6.2 On-Line Testing

Figure 6.5 shows the results from the four weeks of on-line testing. In this figure, data from the Monitek TST-SC and the reference turbidimeters are shown, along with additional data supplied by the Dublin Road Water Plant (DRWP). Data from the DRWP are from a turbidimeter in the plant sampling the same water stream at a different location, for plant operational purposes. These DRWP data are shown to illustrate the trends in turbidity of the water stream sampled for this test. No quantitative comparisons with the DRWP data should be made, since these data were not collected at the same location as samples for this verification test. For convenience, only one data point per hour is shown for the Monitek TST-SC although data were recorded at intervals of 10 seconds throughout the on-line testing. Breaks in the data from the Monitek turbidimeter indicate periods during which the turbidimeter was taken off-line for calibration checks, or cleaning.

In general, this figure illustrates correlation and sometimes close quantitative agreement between the Monitek and the reference measurements. Also, the varying turbidity levels shown by the TST-SC indicate a temporal pattern similar to that of the DRWP data. Two episodes near the end of the four week period show large deviations from the benchtop measurements by the Monitek turbidimeter. These episodes occurred after adjustments to the recirculation system and are likely to be associated with these modifications. Consequently, the data from October 4 through 5 and the data from October 13 through 14 will not be included in the following discussions of accuracy.

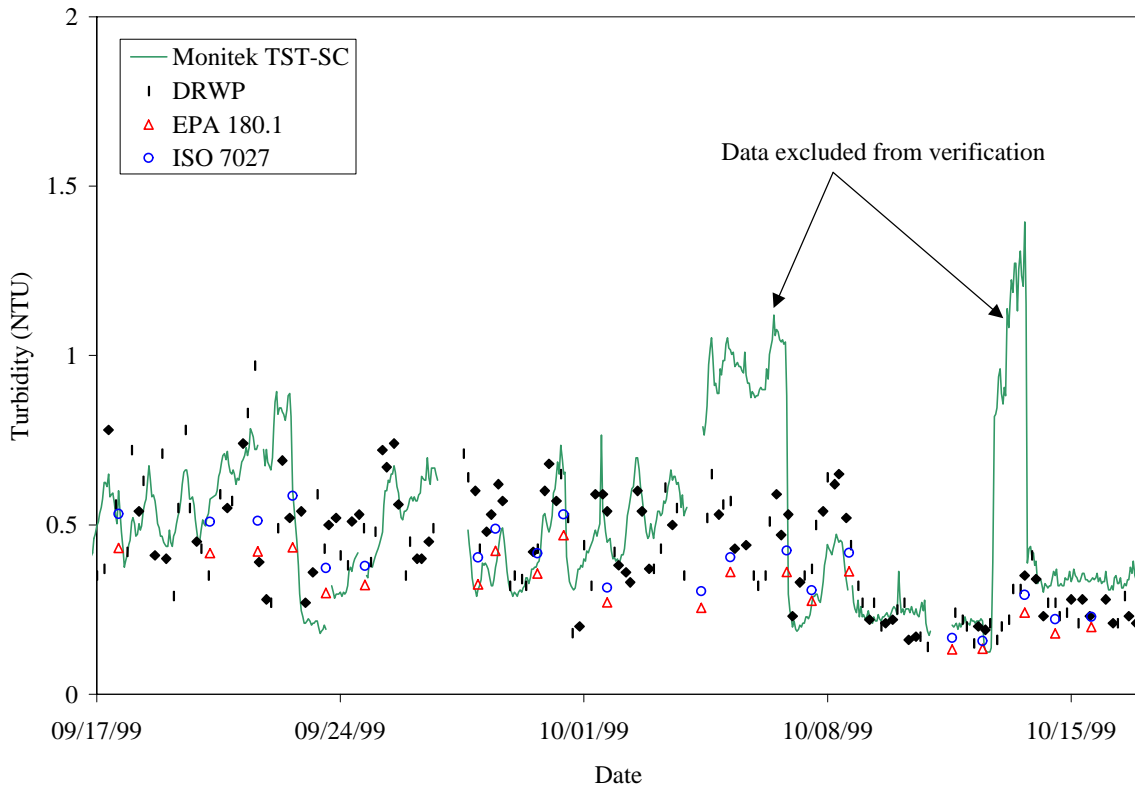


Figure 6-5. Summary of Stream Turbidity Data from On-Line Testing of Monitek TST-SC

6.2.1 Accuracy

The results from the four weeks of on-line accuracy testing are given in Table 6-8 and plotted in Figure 6-5. The results shown in the table are given as the average of the two simultaneous readings taken each day on samples from the plant water stream with the Monitek TST-SC turbidimeter and the reference turbidimeters. In cases where more than the prescribed two readings were recorded, all the values are included in the reported average. Additionally, the bias in the Monitek readings relative to the reference turbidimeters is reported.

The verification results in Table 6-8 show that the Monitek TST-SC generally agreed with the ISO 7027 reference turbidimeter within approximately 0.1 NTU. Positive and negative biases of up to about 50% characterize most of this data range. The TST-SC and reference data exhibited a linear regression of the form $TST-SC = 1.113 (ISO 7027) + 0.050 \text{ NTU}$ with $r^2 = 0.534$.

The secondary comparison in Table 6-8 shows somewhat lower accuracy of the TST-SC relative to Method 180.1, as expected. The linear regression has the form $TST-SC = 1.306 (\text{Method } 180.1) + 0.057 \text{ NTU}$, with $r^2 = 0.463$.

Table 6-8. On-Line Daily Accuracy Check Results

| Date | Monitek TST-SC NTU | Verification Results^a (Relative bias %) | Secondary Comparison^b (Relative bias %) |
|-------------|---------------------------|---|---|
| 9/17/99 | 0.5854 | 0.5320 (10.0) | 0.4315 (35.7) |
| 9/20/99 | 0.6860 | 0.5090 (34.8) | 0.4165 (64.7) |
| 9/21/99 | 0.7441 | 0.5115 (45.5) | 0.4215 (76.5) |
| 9/22/99 | 0.8081 | 0.5855 (38.0) | 0.4338 (86.3) |
| 9/23/99 | 0.3534 | 0.3725 (-5.1) | 0.2990 (18.2) |
| 9/24/99 | 0.4145 | 0.3790 (9.4) | 0.3220 (28.7) |
| 9/27/99 | 0.8844 | 0.4040 (118.9) | 0.3245 (172.5) |
| 9/28/99 | 0.5029 | 0.4885 (2.9) | 0.4230 (18.9) |
| 9/29/99 | 0.4175 | 0.4155 (0.5) | 0.3560 (17.3) |
| 9/30/99 | 0.6433 | 0.5310 (21.1) | 0.4690 (37.2) |
| 10/1/99 | 0.4633 | 0.3140 (47.5) | 0.2710 (70.9) |
| 10/6/99 | 0.3809 | 0.4240 (-10.2) | 0.3605 (5.6) |
| 10/7/99 | 0.2588 | 0.3065 (-15.6) | 0.2755 (-6.1) |
| 10/8/99 | 0.2934 | 0.4173 (-29.7) | 0.3627 (-19.1) |
| 10/11/99 | 0.1978 | 0.1660 (19.1) | 0.1320 (49.8) |
| 10/12/99 | 0.2283 | 0.1570 (45.4) | 0.1340 (70.4) |
| 10/15/99 | 0.3779 | 0.2280 (65.7) | 0.1985 (90.4) |
| 10/18/99 | 0.3809 | 0.1900 (100.5) | 0.1830 (108.1) |

^a Comparison with ISO 7027 reference method (2100AN IS reference turbidimeter).

^b Comparison with EPA Method 180.1 (2100AN reference turbidimeter).

A similar positive bias was observed for all of the on-line turbidimeters tested in this verification test, suggesting a systematic bias in the reference data. It should be noted that, since visible granular deposits accumulated in the test apparatus during the on-line testing, it is possible that a systematic negative bias may have existed as a result of large particles settling in the grab sample vial between sample collection and reference analysis.

6.2.2 Drift

6.2.2.1 Calibration Checks

The results from the twice-weekly calibration checks at 0.5 NTU are shown in Figure 6-6 and summarized in Table 6-9. The results from these calibration checks indicate a negative bias of the Monitek TST-SC turbidimeter relative to the ISO 7027 reference turbidimeter, which is consistent with the results of the linearity test and accuracy calculations discussed in Sections 6.1.1 and 6.1.2, respectively.

However, on several occasions the results from the Monitek TST-SC turbidimeter indicated a positive bias with respect to the reference turbidimeter. A review of the data suggested that perhaps fouling of the optics had caused a positive shift in the readings. When shifts of this nature were observed, either from the calibration checks, or from the daily accuracy readings discussed in Section 6.2.1, the Monitek TST-SC turbidimeter was taken off-line for cleaning. For the final calibration check on October 18, two sets of measurements were recorded. One set was recorded before cleaning of the turbidimeter and showed no significant bias relative to the reference turbidimeter. The second set was recorded after cleaning and showed a negative bias of approximately 20 to 25% relative to the reference reading. These results strongly suggest that the observed positive shifts in the Monitek readings were caused by optics fouling. After cleaning the optics, positive shifts of this nature were eliminated and agreement with other calibration checks was observed.

The secondary comparison in Table 6-9 shows essentially the same behavior relative to the Method 180.1 data as was observed relative to the ISO 7027 reference data.

6.2.2.2 Final Linearity Check

Data from the final linearity check are shown in Figure 6-7a. These data were recorded after completion of the four weeks of on-line testing and after the Monitek TST-SC turbidimeter had been cleaned. As with the data from the initial linearity test, these data, excluding readings for the < 0.1 NTU water, were analyzed by linear regression. The results are summarized in Table 6-10. In Table 6-11, the results of the final linearity test are compared with those from the initial linearity check conducted at the start of the verification as part of the off-line phase.

The verification results of the regression analysis (Table 6-10) show a high degree of linearity, with a slight negative bias in the slope with respect to the reference turbidimeter, and a small negative intercept of approximately 0.1 NTU.

The verification results in Table 6-11 show a change of only 0.3% in the slope of the TST-SC response relative to the ISO 7027 reference method between the initial and final linearity tests. Similarly, the change in intercept shown in Table 6-11 (0.005 NTU) is very small. Based on the results of the daily calibration checks, the average difference between the reference turbidimeter readings and the stated turbidity value of the formazin standard used for the checks was 3.2%, with a standard deviation of 2.4%. With these uncertainties, at the 95% confidence level, the

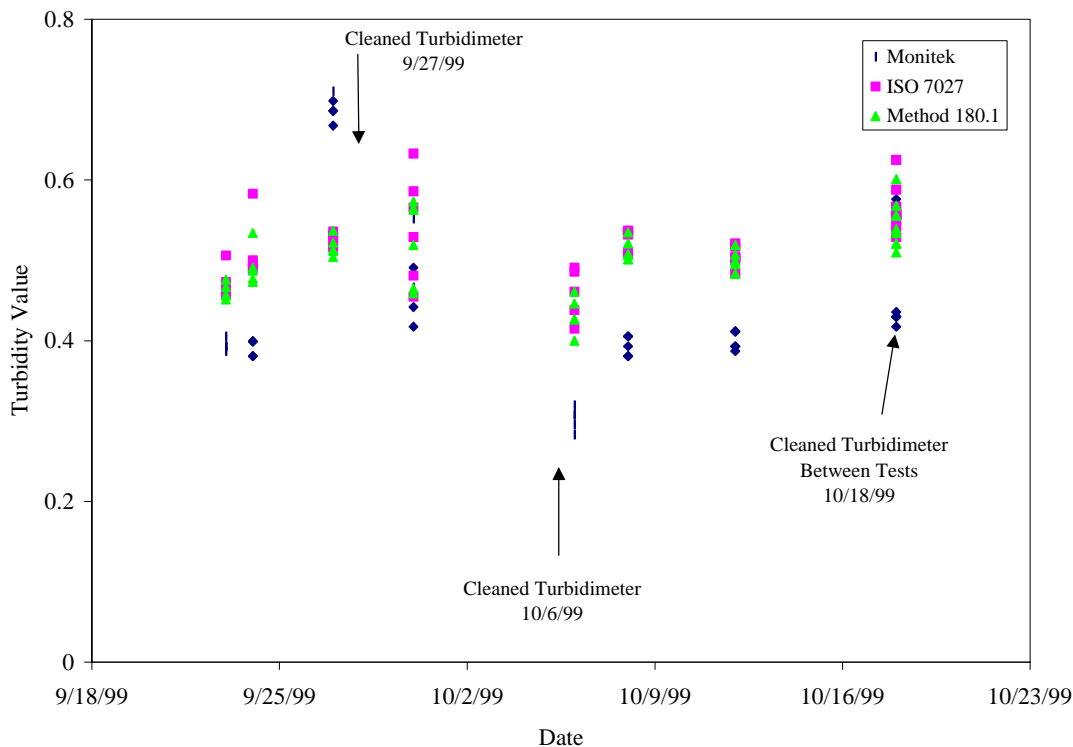


Figure 6-6. Twice-Weekly Calibration Checks During On-Line Testing of the MonitekTST-SC Turbidimeter

Table 6-9. Results of Calibration Checks Performed During On-Line Testing

| ate | Monitek TST-SC (NTU) | Verification Results ^a (Relative Bias %) | Secondary Comparison ^b (Relative Bias %) |
|----------|----------------------|---|---|
| 09/23/99 | 0.394 | 0.473 (-16.7) | 0.461 (-14.5) |
| 09/24/99 | 0.392 | 0.512 (-23.5) | 0.492 (-20.4) |
| 09/27/99 | 0.690 | 0.526 (31.1) | 0.518 (33.2) |
| 09/30/99 | 0.482 | 0.542 (-11.1) | 0.524 (-8.1) |
| 10/06/99 | 0.303 | 0.458 (-33.9) | 0.432 (-29.9) |
| 10/08/99 | 0.393 | 0.530 (-25.8) | 0.514 (-23.6) |
| 10/12/99 | 0.401 | 0.505 (-20.5) | 0.498 (-19.4) |
| 10/18/99 | 0.560 | 0.556 (0.8) | 0.544 (3.0) |
| 10/18/99 | 0.428 | 0.569 (-24.7) | 0.544 (-21.3) |

^a Comparison with ISO 7027 reference method (2100AN IS reference turbidimeter).

^b Comparison with EPA Method 180.1 (2100AN reference turbidimeter).

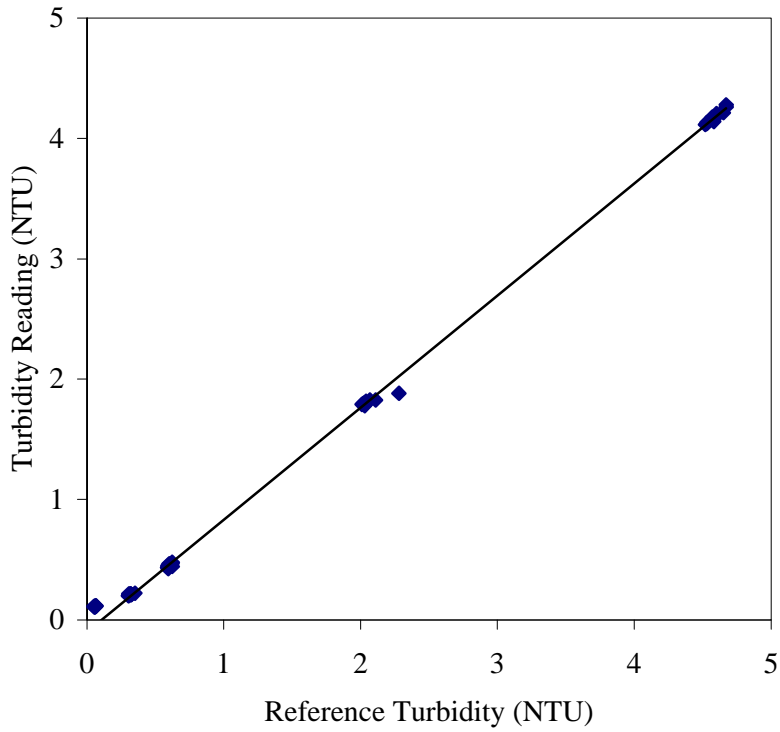


Figure 6-7a. Final Linearity Plot for Monitek TST-SC vs. ISO 7027 Reference Turbidimeter

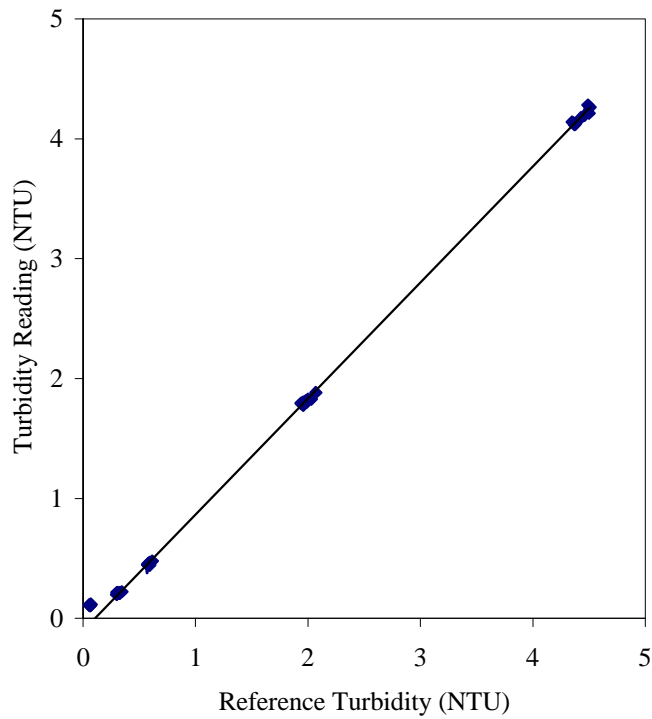


Figure 6-7b. Final Linearity Plot for Monitek TST-SC vs. Method 180.1 Reference Turbidimeter

Table 6-10. Statistical Results of Final Linearity Test

| Linear Regression | Reference Turbidimeter | |
|----------------------------|-----------------------------------|-----------------------------------|
| | Verification Results ^a | Secondary Comparison ^b |
| Slope (std. error) | 0.932 (0.003) | 0.967 (0.002) |
| Intercept (std. error) NTU | -0.102 (0.007) | -0.104 (0.004) |
| r ² | 0.9998 (0.0289) | 0.9999 (0.0176) |

^a Comparison with ISO 7027 reference method (2100AN IS reference turbidimeter).

^b Comparison with EPA Method 180.1 (2100AN reference turbidimeter).

Table 6-11. Comparison of Results from Linearity Tests at Beginning and End of the Verification Test

| | Verification Results ^a | | Secondary Comparison ^b | |
|------------------------|-----------------------------------|-----------------|-----------------------------------|-----------------|
| | Slope | Intercept (NTU) | Slope | Intercept (NTU) |
| Initial Linearity Test | 0.935 | -0.107 | 0.946 | -0.089 |
| Final Linearity Test | 0.932 | -0.102 | 0.967 | -0.104 |
| Difference | -0.003 | 0.005 | 0.021 | -0.015 |
| % Difference | - 0.3 | – | 2.2 | – |

^a Comparison with ISO 7027 reference method (2100AN IS reference turbidimeter).

^b Comparison with EPA Method 180.1 (2100AN reference turbidimeter).

initial and final slopes are not significantly different from unity, and no drift can be inferred from the difference between the slopes. The small difference in intercept is also insignificant.

The secondary comparison shown in Table 6-11 leads to a similar conclusion, as a change in the regression slope of only 2.2% was observed, relative to Method 180.1

6.3 Other Performance Parameters

6.3.1 Cost

As tested, the cost of the Monitek TST-SC was approximately \$1,000.

6.3.2 Maintenance/Operational Factors

The Monitek TST-SC is designed for in-line or submersible operation. As tested the Monitek TST-SC turbidimeter was configured for direct in-line pipe mounting. Time requirements for installation were not assessed in this test, as temporary installation in the test apparatus did not reflect the permanent installation in a water treatment facility. After installation, the Monitek TST-SC required no operator input and provided data continuously throughout the verification test.

The main limitation of the Monitek TST-SC is the necessity for off-line cleaning. During the off-line testing no cleaning was required, presumably because of the relative cleanliness of the samples being tested. During the on-line testing, the Monitek TST-SC turbidimeter required cleaning after approximately a week of operation.

Chapter 7

Performance Summary

The Monitek TST-SC is an on-line turbidimeter designed to provide continuous, real-time measurement of the turbidity of aqueous solutions. The Monitek TST-SC turbidimeter provided linear response over the tested range from 0.3 to 5 NTU. The TST-SC does not respond to turbidity levels below ~ 0.1 NTU, and the response of the TST-SC turbidimeter was not measured above 5 NTU in this test. The slope of the response curve for the Monitek TST-SC turbidimeter relative to the ISO 7027 reference turbidimeter was 0.935 at the beginning of the test, with an intercept of - 0.107 and $r^2 > 0.999$.

The TST-SC turbidimeter showed a negative bias relative to the reference turbidimeter in measuring standard solutions. The observed negative bias ranged from ~ 30% at 0.3 NTU to ~ 8% at 5 NTU. This bias is consistent with the observed response curve slope of less than unity. Much of the observed bias can be accounted for by the small negative intercept (~ -0.1 NTU). A shift in the calibration curve to eliminate the intercept would dramatically improve the apparent relative accuracy of the Monitek TST-SC turbidimeter. Measurement precision of the Monitek TST-SC was approximately the same as for the ISO 7027 reference turbidimeter throughout the range of turbidity measured in this test. The precision ranged from 3.3% RSD at 0.3 NTU to 0.35% RSD at 5 NTU.

Water temperature has a small effect on the response of the Monitek TST-SC turbidimeter at low turbidity (0.3 NTU), but no effect at higher turbidity (5 NTU). The effect at 0.3 NTU amounts to a decrease in observed turbidity of 0.4% per degree C relative to the ISO 7027 reference turbidimeter. A small effect of color on readings was found at low turbidity (~ 0.1 NTU), but none at higher turbidity (5 NTU). However, the low turbidities used in this test approach the 0.1 NTU lower response limit of the TST-SC, and consequently, it is unclear whether the observed effect is in fact a response to color. In the 0.1 to 1.0 gpm range of flow rates tested for the Monitek TST-SC turbidimeter, no statistically significant effect was found on the turbidity readings as a function of sample flow rate.

In reading the turbidity of treated, unfiltered water from a municipal drinking water plant, the Monitek TST-SC turbidimeter generally showed a positive bias of 0.1 to 0.2 NTU relative to the reference turbidimeter readings of 0.1 to 0.6 NTU. This bias was observed over much of the four weeks of measurement of the water plant sample stream. However, calibration checks of the Monitek TST-SC turbidimeter, performed using 0.5 NTU formazin standards throughout the same period, indicated a negative bias in the response of the Monitek TST-SC. A systematic bias in the reference readings may have been present in the on-line test phase, and may have

contributed to the observed differences between the Monitek TST-SC and reference readings on stream samples. In addition, fouling of the TST-SC optics during stream sampling may have been a factor; substantial decreases in TST-SC readings were observed when the turbidimeter optics were cleaned.

A change of approximately 0.3% in the slopes of the response curves between the beginning and end of the verification test was observed. This change is well within the experimental uncertainty of the reference measurements and does not indicate a drift in the calibration of the Monitek TST-SC. Similarly, no drift in the intercept of the response curve was observed. As noted above, fouling of the optics during on-line testing caused intermediate drift, which was reversed upon cleaning.

The Monitek TST-SC turbidimeter is easy to use and provides continuous on-line turbidity readings. The turbidimeter was cleaned every 10 to 12 days during the test to remove residues and material deposits from the optics on the inside of the turbidimeter. This was the only maintenance required.

Chapter 8 References

1. “Water Quality—Determination of Turbidity,” *International Standard ISO 7027*, Second Edition, International Organization for Standardization, Geneva, 1990.
2. *Test/QA Plan for Verification of On-Line Turbidimeters*, Battelle, Columbus, Ohio, June 3, 1999.
3. “Determination of Turbidity by Nephelometry,” *Methods for the Determination of Inorganic Substances in Environmental Samples*, Method 180.1, EPA/600/R-93/100, U. S. Environmental Protection Agency, Cincinnati, Ohio, August 1993.
4. “Color in Water by Visual Comparison to Standards,” *Standard Methods for the Examination of Water and Wastewater*, 18th Edition, Method 2120-B, American Public Health Association, 1992.
5. *Quality Management Plan (QMP) for the ETV Advanced Monitoring Systems Pilot*, U.S. EPA Environmental Technology Verification Program, Battelle, Columbus, Ohio, September 1998.

**Appendix A
Data Recording Sheet**

Appendix B
Technical Systems Audit Report