Rapid Multiparameter Analysis of Conductivity, Alkalinity, pH, Fluoride, Color, and Turbidity

Introduction:

The MANTECH multi-parameter system is an effective use of personnel time, sample volume, and reagents. A significant advantage of this system is that it can be run unattended overnight like many of the other MANTECH systems. It can also be configured to minimize time or sample volume used depending on the needs of the customer. Possible tests that can be performed by this system are alkalinity, pH, fluoride, color, turbidity and conductivity or nearly any combination that is required.

Conductivity is a measure of the ability of an aqueous solution to conduct an electric current. It is caused by the movement of ions within a solution that permit the passage of the electrical current. This measure is an excellent indicator of water purity and is used as a mechanism in the determination of water contamination. The lower the conductivity, the purer the sample is. Since conductivity is measured first directly in the sample tube, the non-destructive nature of the analysis permits further studies on the same sample without contamination.

pH is a measure of the relative acidity or basicity of a solution measured on a scale of 0 to 14. It is measured directly by a pH electrode that records the voltage difference between the solution and a reference electrode contained within the probe. The voltage measured from the samples is compared to a previously made calibration curve to determine the H+ concentration. Automating pH is a wise choice because it is a simple, easy method which uses time that could be better spent performing more complicated tests. With this system, pH is measured just prior to the alkalinity titration, while turbidity, color and fluoride are stabilizing.

Alkalinity refers to the acid-neutralizing or buffering capacity of a solution. This method measures the concentrations of hydroxide, carbonate, and bicarbonate, and total alkalinity. It is calculated as the sum of their values, and expressed as mg of $CaCO_3$/L. Unlike a manual titration, the automated method provided by MANTECH does not require the use of indicators to mark endpoints and calculations are all performed without user intervention. With this system, the alkalinity titration is performed while fluoride is being stabilized.

Fluoride concentration is determined by an ion selective electrode. After calibrating with known standards, the sample's response can be compared to the calibration curve and a concentration is determined. Both the standards and the samples are pre-treated with TISAB (Total Ionic Strength Adjuster) to ensure that the background response from each sample is similar. The RapidDuo adds the TISAB to the sample at the start of the method and allows the fluoride to stabilize while taking other measurements to save time.

Color is used as a general indicator of the quality of water, along with turbidity and odor. It is measured in color units (CU) where 1 CU equals 1 ppm of platinum cobalt. A traditional method for color measurement is the visual comparison of samples to standards in Nessler tubes, which is simple and inexpensive, but relies on the sensitivity of the human eye and requires readings by several different people for an acceptable level of precision. This method involves measuring the absorbance of a sample in a flow through cell at a specified wavelength following calibration with known standards.

Turbidity determines the amount of suspended particles in a solution, measured in nephelometric turbidity units (NTU) or nephelometric formazin units (NFU), and is used as a general indicator of the quality of water. This method involves shining light into a sample and recording the light scattered at 90 degrees to the light path.

This multi-parameter system can be configured in different ways to optimize sample volumes required, analysis times and cost. A summary of the different configurations for the Automax122 Autosampler is provided below.

Type of System	Description	Equipment	Estimated Analysis Time*	Automax 122 Sampler Capacity	Benefits
Rapid Duo with Simultaneous Turbidity	All parameters stabilize at the same time	Two TitraSips with 35mL Cells	10 min	47 (125mL cups)	Fastest analysis time of any other configuration
Rapid Duo with Sequential Turbidity	Turbidity is measured first, then all other parameters stabilize at the same time	Two TitraSips with 35mL Cells	12 min	122 (50mL tubes)	Less sample volume required and greater sampler capacity than simultaneous turbidity, and faster than single-Titrasip systems
Single TitraSip with Simultaneous Turbidity	Conductivity is measured first, then turbidity is allowed to stabilize while all other parameters are measured sequentially	One TitraSip with 85mL Cell	14 min	47 (125mL cups)	Less equipment required than dual-Titrasip systems but faster than sequential turbidity
Single TitraSip with Sequential Turbidity	Conductivity and turbidity are measured first then all other parameters are taken sequentially	One TitraSip with 85mL Cell	16 min	47 (125mL cups)	Less equipment required than dual-Titrasip systems and less sample volume used than simultaneous turbidity

*Times of analysis include all pipetting, IntelliRinse rinsing, draining and measurements for all parameters (conductivity, pH, alkalinity, fluoride, turbidity and color). Times are estimated and may vary depending on certain parameter concentrations.

Conforms To:

Parameter	Method Numbers
Alkalinity	EPA Method 310.1 Standard Methods 2320 ASTM Standards Method D 1067-92 ISO 9963-2
pH	EPA Method 150.1 Standard Method 4500-H^+ B ASTM Standards Method D 1293 – 99 ISO 10523
Turbidity	EPA Method 110.2 Standard Method 2130 B ISO 7027
Color	EPA Method 110.2 Standard Method 2120C ISO 7887
Fluoride	EPA Method 340.2 Standard Methods 4500-F- A ISO 10359-1
Conductivity	Standard Methods 2510 B EPA Method 120.1 ASTM Standards Method D1125 AOAC Official Method 957.16 ISO 7888

Sample: All water samples.

Concentration Ranges:

Parameter	Concentration Range	MDL*
pH	1-13	N/A
Alkalinity	0.3-1000 ppm	0.3 ppm
Turbidity	0.05-2000 NTU	0.05 NTU
Color	2-500 CU	2 CU
Fluoride	20ppb-100 ppm	0.02 ppm
Conductivity	1.87-12900 µS	1.87 µS

*The Method Detection Limits (MDL) were determined based on data obtaining a coefficient of variance better than 30%. Measuring ranges were determined by analyzing laboratory-prepared standards. Results may differ depending on laboratory practices and sample matrix.

Apparatus:

1. pH Electrode (PCE-80-PH1013)
2. Fluoride ion selective electrode (PCE-80-FL1001)
3. 2x Electrode Cable (PCE-86-EX1001)
4. Interface (PC-1000-102/4)
5. Burivar I/2 (PC-1104-00)
6. TitraRinse pump (PC-1000-408)
7. 2x Titra-Sip Modules (PC-1300-475)
8. Turbidity meter (PC- 1000-130).
    a. White light Turbidity meter option (PC-20014)

b. Infrared Turbidity meter option (PC-20016)
9. Reversible Peri-Max pump (PC-1000-475)
10. UVmini 1240 Spectrophotometer (PC-206-24000-92) and accessories including Titra-Rinse 250 ml/min pump (PC-1000-400), 50 mm flow cell (PC-1000-811)
11. Conductivity/TDS Meter, Model 4510 (PCM-1000-991)
12. Autosampler
    a. STANDARD, 73 sample locations (PC-1000-681)
    b. LARGE, 122 sample locations (PC-1000-688)
    c. MEGA, 197 sample locations (PC-1000-680)

Reagents:

1. Standard sulphuric acid titrant, 0.02 N
2. Sodium carbonate solution: 1000 ppm alkalinity= 1.0589 g Na_2CO_3 in 1L distilled water. Dilute as necessary for other concentrations
3. pH 4, 7, and 10 buffer solutions
4. 0.02 to 100 NTU: Calibration Kit 1 (PC-1000-139)
5. 0.02 to 1750 NTU: Calibration Kit 2 (PC-1000-140)
6. Color Calibration stock solution (500 CU): In a 1 L volumetric flask, add 1.246 g Potassium Chloroplatinate and 1.0 g Cobaltous Chloride to 100 mL Hydrochloric Acid and fill to 1000 mL with de-ionized water. This solution is also commercially available. Dilute from the 500 CU stock solution as needed
7. Total Ionic Strength Adjustment Buffer (TISAB).
8. Standard Potassium Chloride Solution (KCl): 7.455 g in 1 L for 12,900 µS standard (0.1 N). Dilute for other concentrations
9. 1000 ppm F^- standard (2.21 g of NaF into 1 L deionized water). Dilute for lower standards

Procedure:

Conductivity Calibration:

1. Place calibration standards into autosampler rack in ascending order.
2. The conductivity cell will be rinsed with DI water in the rinse station.
3. The cell will move to the first standard and be dipped 3 times in the solution, remaining fully immersed on the third dip.
4. The solution will stabilize for 25 seconds and the conductivity reading recorded.
5. The cell will be rinsed again with DI water.
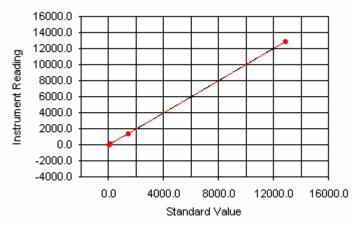6. Steps 3-5 are repeated for the remaining calibration standards.

Figure 5: Sample Conductivity Calibration Curve

pH Calibration:

1. Place pH 4, 7, and 10 buffers into the autosampler rack and run a schedule to calibrate the pH probe.
2. The sampler will move to the rinse station where the sample transfer line and Titrasip vessel are rinsed with deionized water.
3. The sampler will move to the pH 4 buffer position and the sample transfer line will be primed with the pH 4 buffer solution.
4. 10 mL of buffer solution will be pumped into the Titrasip cell and the stirrer is turned on.
5. The pH of the buffer solution is measured and recorded.
6. Steps 2 to 5 will be repeated for the pH 7 and 10 buffer solutions.
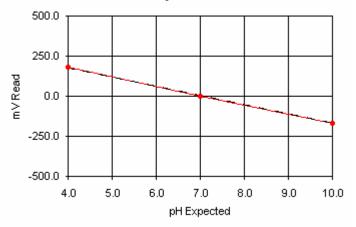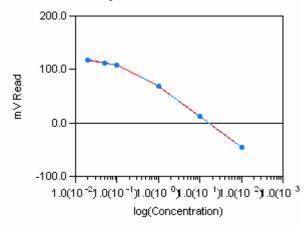7. The calibration curve will be calculated and reported.

Figure 1: Sample pH Calibration Curve

Fluoride Calibration:

1. Place calibration standards that cover the range of values predicted for your samples into the sampler rack in ascending order and run a schedule to calibrate the fluoride probe.
2. The sampler will move to the rinse station where the sample transfer line and Titrasip vessel are rinsed with deionized water.
3. The sampler moves to the first standard position.
4. The sample transfer line is primed with the standard solution.
5. 5 mL of the standard and 5 mL of TISAB is pumped into the Titrasip vessel, and the stirrer is turned on.
6. The fluoride concentration is measured and recorded.
7. Steps 2-6 are repeated for the remaining standards.
8. The calibration curve is calculated and reported.

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Color Calibration:

1. Place calibration standards in ascending order in the autosampler rack.
2. The sampler will move to the rinse station and DI water will be pumped through the flow cell to rinse the tubing and the cell.
3. The sampler will then move into the first standard and 15 mL of standard will be pumped through the flow cell.
4. The spectrophotometer is allowed to stabilize for 30 seconds, and then the absorbance at 410 nm is recorded.
5. The flow cell is rinsed using the IntelliRinse system with 2.5 mL of air pumped through the flow cell between each rinse.
6. Steps 2-5 are repeated for the remaining calibration standards, following which a calibration curve is generated and reported.
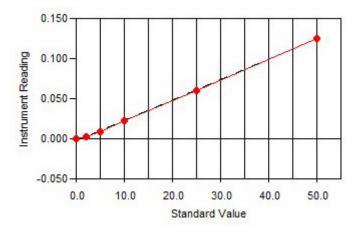

Figure 3: Sample Color Calibration Curve

Turbidity Calibration:

1. Place calibration standards in ascending order in the autosampler rack.
2. The sampler will move to the rinse station and DI water will be pumped through the flow cell to rinse the tubing and the cell.
3. The sampler will then move into the first standard and 25 mL of standard will be pumped through the flow cell.
4. The turbidity meter will stabilize for 60 seconds, and the turbidity reading recorded.
5. The sample will be pumped back into the tube and the sampler moves to the rinse station to rinse the flow cell and tubing.
6. Steps 2-5 are repeated for the remaining calibration standards, following which a calibration curve is generated and reported.
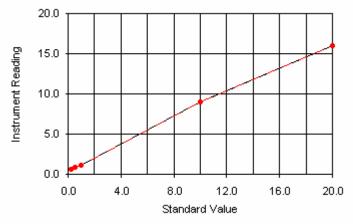
Figure 4: Sample Calibration Curve for Turbidity

Sample Analysis:
*Please note that this bulletin describes a Rapid Duo with Simultaneous Turbidity system set-up.

1. Place a minimum of 75 mL of sample into the autosampler rack.
2. The sampler will move to the rinse station where all sample transfer lines are rinsed with deionized water.
3. Color Intelli-Rinse is performed starting with a color reading to ensure the rinse water measures below an absorbance of 0.002. If the absorbance is too high, 2.5mL of air is pumped through the spectrophotometer, and then another rinse of the color system is performed. This step repeats until the color reading of the rinse water is below the specified value or 6 rinses are reached, whichever comes first.
4. 2.5mL of air is pumped through the spectrophotometer to avoid dilution of the sample with rinse water.
5. The sampler moves to the first sample and the conductivity probe is dipped 3 times in the solution, remaining fully immersed on the third dip.
6. The conductivity probe is allowed to stabilize and the reading is recorded.
7. The transfer lines will be primed with sample and the TitraSip cells are rinsed and drained.
8. The stirrers located on the sampler arm and in the TitraSip cells are turned on, and sample solution will be pumped into the spectrophotometer, turbidity meter, and Titrasip cells simultaneously.
9. 5mL of TISAB is added to the TitraSip vessel containing the fluoride probe.
10. The pH of the sample is measured and recorded, while the turbidity meter, spectrophotometer and fluoride probe are stabilizing.
11. The turbidity and color readings are recorded.
12. The sample is titrated with standard sulphuric acid titrant to pH 4.2, and the alkalinity of the sample is calculated, including all species (palk, talk, carbonate, bicarbonate, and hydroxide).
13. The fluoride probe is considered to be stable at this point so the reading is taken immediately.
14. The sample in the turbidity flow cell is pumped back into the sample tube.
15. The TitraSip cells are drained and rinsed with deionized water, along with all transfer lines. The color Intelli-Rinse is performed prior to moving to the next sample.
16. Steps 2 to 15 are repeated until all samples are complete.
17. The TitraSip cells are filled with the appropriate electrode storage solutions.
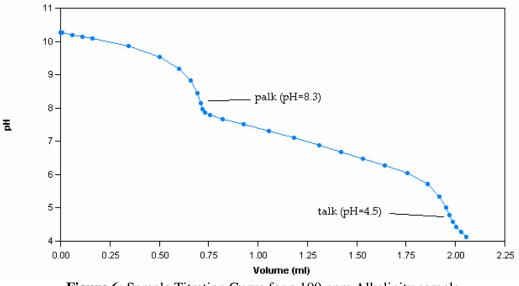18. A water analysis report is generated at the conclusion of the run.

Figure 6: Sample Titration Curve for a 100 ppm Alkalinity sample

Calculations:

Color, Fluoride, pH, *Conductivity and Turbidity* are measured directly so no calculations are necessary.

Alkalinity:

Alkalinity calculation for phenolphthalein alkalinity (palk)

Function	Expression	Result
palk (P)	$= \dfrac{xvol(8.3) * tcon * 50\,000}{svol}$	mg $CaCO_3$ / L

xvol(8.3)=	volume of standard acid titrant used to titrate to pH 8.3
tcon=	normality of titrant (N)
50 000=	equivalent weight of $CaCO_3$ as defined in the methods[8]
svol=	volume of sample titrated (mL)

Alkalinity calculation for total alkalinity (talk)

Function	Expression	Result
talk (T)	$= \dfrac{xvol(4.5) * tcon * 50\,000}{svol}$	mg $CaCO_3$ / L

xvol(4.5)=	volume of standard acid titrant used to titrate to pH 4.5
tcon=	normality of titrant (N)
50 000=	equivalent weight of $CaCO_3$ as defined in the methods[8]
svol=	volume of sample titrated (mL)

Alkalinity calculation for potentiometric titration using low-level method*

Function	Expression	Result
talk (T)	$= \dfrac{[2 * xvol(4.5) - xvol(4.2)] * tcon * 50\,000}{svol}$	mg $CaCO_3$ / L

xvol(4.5)=	volume of standard acid titrant used to titrate to pH 4.5
xvol(4.2)=	volume of standard acid titrant used to titrate to pH 4.2
tcon=	normality of titrant (N)
50 000=	equivalent weight of $CaCO_3$ as defined in the methods[8]
svol=	volume of sample titrated (mL)

*Low-level alkalinity method is only used for samples with alkalinity values calculated at less than 20 ppm.

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Results for P and T alkalinity offer a means for stoichiometric classification of the hydroxide, carbonate, and bicarbonate forms of alkalinity.

- Hydroxide (OH^-) alkalinity is present if *palk* is more than half the *talk*
- Carbonate (CO_3^{2-}) alkalinity is present when *palk* is not zero but is less than *talk*
- Bicarbonate (HCO_3^-) ions are present if *palk* is less then half the *talk*

Table 1: Alkalinity Calculations

Result of Titration	Hydroxide (OH^-) Alkalinity as $CaCO_3$	Carbonate (CO_3^{2-}) Alkalinity as $CaCO_3$	Bicarbonate (HCO_3^-) Alkalinity as $CaCO_3$
P = 0	0	0	T
P < 1/2T	0	2P	T – 2P
P = 1/2T	0	2P	0
P > 1/2T	2P – T	2(T – P)	0
P = T	T	0	0

Quality Control:

The table below presents a summary of the average value, standard deviation and %RSD for a tap water sample analyzed for all parameters.

Parameter	pH	Total Alkalinity	Conductivity	Fluoride	Color	Turbidity
Average	7.97	270.09	896.24	0.73	153.02	0.01
RSD	0.01	0.86	4.12	0.02	2.63	0.0003
% RSD	0.12%	0.32%	0.46	2.77	1.72	28.75

Hints/Suggestions:

1. Specialized electrodes may be required depending on the ionic strength of the samples.
2. Before every run, ensure the appropriate electrode fill solutions are just below the fill holes.
3. A calibration of each parameter should be performed prior to every run of samples for best results. In addition, a zero should be done before a color calibration. Calibration standards used should cover and extend past the range of expected readings of your samples.
4. After every run or when the electrodes are not in use, store in the appropriate storage solutions indicated in the electrode manuals. This is recommended in order to keep the electrodes hydrated and conditioned to maximize lifespan.
5. After six months to a year, it is recommended that electrodes be replaced.
6. It is recommended that quality control standards be included in each sample rack to monitor the accuracy of the analysis.
7. Turbidity samples degrade over time and so they must be analyzed as soon as possible. If storage overnight is required, then it is recommended that the samples be refrigerated at 4 degrees Celsius. These samples must then be allowed to reach room temperature in order to avoid condensation on the surface of the glass turbidity cell.
8. The Infrared Turbidity meter is recommended for use with yellow colored samples and ISO/EN method conformance.
9. The TISAB solution added to samples for fluoride analysis should be in a 1:1 ratio with the sample volume.
10. Proper insertion of the conductivity cell is crucial to remove air bubbles, reduce carryover, and ensure accurate conductivity measurements. This is successfully achieved by triple dipping the conductivity cell into the solution. Studies using a single dip revealed a noticeable decrease in accuracy and precision.