Application Note #127 – IntelliVol™

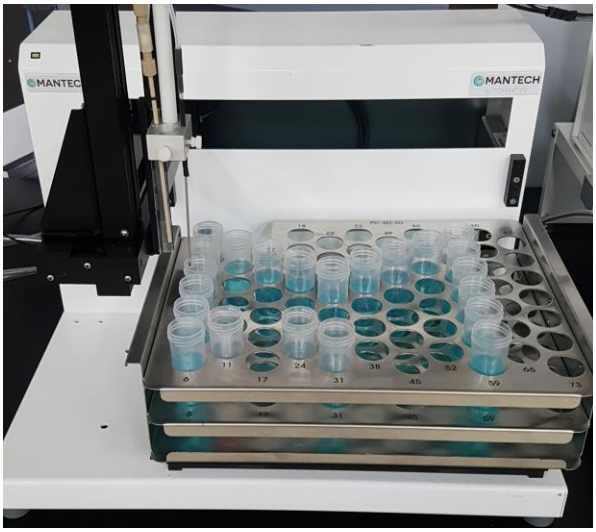
Updated December 2019

Introduction:

IntelliVol™ is a MANTECH Innovation for MT Automated Environmental titration systems. It eliminates the requirement for manual pipetting or for automated pipetting via the TitraSip™ module. It consists of an AM series autosampler, a peristaltic pump, and a needle at a fixed height on the AM sampler Z-arm. The autosampler moves to the sample at the specified height and draws sample from the sample vessel until the height of the needle is reached, thus giving you the same volume every time. Once the calibrated volume remains, the autosampler moves down into the sample and analysis begins. This system can be used with a variety of different sample vessels and can be adjusted for different volumes using MANTECH software. Most titration and Ion Selective Electrode (ISE) Direct Measurement methods can be carried out using IntelliVol™ as a volume determination system. Examples include alkalinity, acidity, total hardness, fluoride and ammonia. The application note describes IntelliVol™ use for automated alkalinity analysis illustrating performance. For details about the alkalinity method, conformance and reagents please see the application abstract 72.

The volume remaining in the sample vessel will need to be calibrated and adjusted in the schedules. This can be done in two ways. Firstly, mass can be used. Five empty vessels are weighed and then filled with deionized water above the volume that is desired. The autosampler will go to the five vessels and draw water out to the needle height. The remaining deionized water can be measured by subtracting the mass of the full vessel by the mass of the empty vessel. Assuming 1 mL deionized water weighs 1 g these masses are averaged and the volume remining is given. The second method involves titrating a standard. Firstly, fill three vessels with a standard of known concentration. Then using a titrant of known concentration, the autosampler will go to each standard, then it will draw out sample to the needle height, then it will titrate the standard to the desired endpoint, and finally it will do a calculation using standard concentration and titrant concentration to determine the volume of the sample in the vessel. Calibrations are recommended every 3 months or as needed.

IntelliVol™ is an add on to MT-10 and MT-30 systems. It can be used for a wide variety of different titration methods and follows approved methods. IntelliVol™ is a simple, fast, and accurate alternative to manual pipetting. Scientists can free pour all their samples into the analysis vessels. It can save time, improve working conditions and worker efficiency. To learn more about IntelliVol™ contact your local Mantech Dealer.



AM73 Series Autosampler

Peristaltic Pump for Sample Aspiration

Probe Holder with Fixed Needle at Specific Height

Sample: All water samples

Apparatus:

1. MT-10, MT-30 or MT-100 Models
2. pH/ISE Electrode* and cable
3. MANTECH Buret (if a titration method is being used)
4. Peristaltic Pump
5. Autosampler: All MANTECH AutoMax Samplers are available with the IntelliVol™ Option

*For IntelliVol™ testing a pH electrode was used and alkalinity samples were measured

IntelliVol™ Calibration (Mass):

1. Label and weigh five empty cups, record the masses.
2. Fill the five cups with deionized water above the needle height.
3. The autosampler will move to each cup and draw water out to the needle height.
4. Weigh the five full cups and subtract the masses of the empty cups.
5. Enter the masses of the remaining deionized water into the popup menus in the Mantech

software.

6. The software will show a report of all the masses entered and the average mass to be used as the IntelliVol™ volume.

IntelliVol™ Calibration (Standard):

1. Fill three cups with a 100 ppm alkalinity standard above the needle height.
2. The autosampler will move to rinse station where the electrode is rinsed with deionized water (if applicable).
3. The autosampler will move to the first standard and draw out sample to the needle height
4. The autosampler will lower into the sample and titrate the sample
5. Steps 2-5 are repeated for the other 2 standards
6. Mantech Software will calculate the volume of the standard
7. A report will show up with the 3 volumes of the vessels and the average of these volumes

Sample Analysis:

1. Free pour >50 mL sample into the sample cup
2. The sampler will move to the rinse station where the electrode is rinsed with deionized water (if applicable).
3. The sampler will move to the first sample position.
4. The IntelliVol™ system will draw out sample to the needle height and then lower into the remaining sample for analysis.
5. The sample will be titrated with standard sulphuric acid titrant to pH 4.2. This is done to ensure that information for low-level alkalinity calculations is available when necessary.
6. The total alkalinity of the sample is calculated and reported.
7. Steps 2 – 6 are repeated for each of the remaining samples.

*Note the volumes described above will vary by configuration

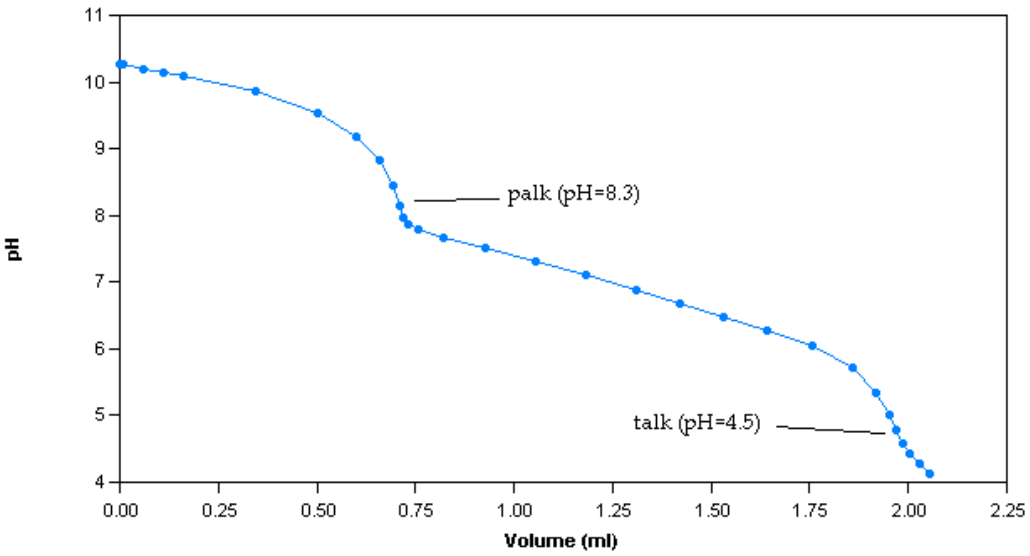


Figure 2: Sample Titration Curve for a 100ppm sample

Calculations:

IntelliVol™ Volume using Mass:

Function	Expression	Result
svol	$= \frac{\text{mass (1) + mass (2) + mass (3) + mass (4) + mass (5)}}{5}$	g (mL)

Mass(x)= mass of deionized water in sample vessel x

IntelliVol™ Volume using Standard:

Function	Expression	Result
svol	$= \frac{\text{xvol(4.5) * tcon * 50 000}}{\text{scon}}$	g (mL)

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
scon= concentration of standard (ppm)

*For more information on alkalinity titrations see application note 72

Quality Control:

Results of 3 tests are shown. The first is consistency of calibrations using different vessels and volumes. The second is 5 replicates of a 10 ppm, 100 ppm and 1000 ppm sample. The third is the consistency of results over time.

Calibration Consistency:

*Means, Standard Deviations, and % CV are shown for each individual day (n=3) and for all results over time

15 mL in a 50 mL sample tube:

Date	Sept 23	Sept 24	Sept 24	μ_{OT}	σ_{OT}	% CV_{OT}
μ_d	15.62	15.18	15.17	15.33	0.211	1.38
σ_d	0.215	0.544	0.522			
% CV_d	1.38	3.58	3.44			

30 mL in a 50 mL sample tube:

Date	Sept 19	Sept 20	Sept 23	μ_{OT}	σ_{OT}	% CV_{OT}
μ_d	28.93	28.83	28.97	28.91	0.058	0.20
σ_d	0.261	0.259	0.186			
% CV_d	0.90	0.90	0.64			

30 mL in a 125 mL sample cup:

Date	Sept 24	Sept 25	Sept 26	μ_{OT}	σ_{OT}	% CV_{OT}
μ_d	31.17	30.96	30.58	30.90	0.242	0.78
σ_d	0.199	0.146	0.430			
% CV_d	0.64	0.47	1.40			

50 mL in a 125 mL sample cup:

Date	Oct 2	Oct 23	μ_{OT}	σ_{OT}	% CV_{OT}
μ_d	51.24	52.41	51.83	0.582	1.12
σ_d	0.778	0.131			
% CV_d	1.52	0.25			

Alkalinity Standard Samples for 5 Replicates:

10 ppm Alkalinity Sample:

<u>Control Limits – Individuals</u>
μ = 9.63
σ = 0.121
% CV = 1.26 %

<u>95% Confidence Limits</u>
μ-2σ = 9.388
μ+2σ = 9.872

<u>99.7% Confidence Limits</u>
μ-3σ = 9.267
μ+3σ = 9.993

100 ppm Alkalinity Sample:

Control Limits – Individuals	95% Confidence Limits	99.7% Confidence Limits
μ = 99.25	μ-2σ = 97.288	μ-3σ = 96.307
σ = 0.981	μ+2σ = 101.212	μ+3σ = 102.193
% CV = 0.99 %		

1000 ppm Alkalinity Sample:

Control Limits – Individuals	95% Confidence Limits	99.7% Confidence Limits
μ = 983.10	μ-2σ = 966.06	μ-3σ = 957.54
σ = 8.520	μ+2σ = 1000.14	μ+3σ = 1008.66
% CV = 0.87 %		

Calibration Validity Test over 2 months:
Four sets of samples were run periodically for 3 replicates over 2 months to determine the validity and consistency of the calibration. The samples run were 100 ppm standard, 10 ppm standard, tap water, and a surface water sample.

Table 2: Summary of consistency of calibration over 2 months

Sample	100 ppm	10 ppm	Tap Water	Surface Water
02-Oct	96.58	9.38	283.69	183.55
04-Oct	97.81	9.15	288.91	186.16
08-Oct	97.77	9.11	283.57	189.35
10-Oct	95.43	9.41	287.14	183.85
15-Oct	94.26	9.15	286.17	182.40
17-Oct	97.79	9.98	294.50	190.21
23-Oct	99.83		308.52	192.27
25-Oct	100.33	10.66	303.36	190.75
29-Oct	98.23	10.58	300.03	189.24
31-Oct	98.70	10.13	308.60	192.62
06-Nov	99.45		300.43	193.59
07-Nov	97.15		299.60	195.25
12-Nov	96.45	9.85	299.84	193.00
14-Nov	96.24	9.74	295.05	189.18
19-Nov	98.77		296.52	190.48
21-Nov	98.16		298.89	188.79
26-Nov	100.39	10.61	304.40	188.44
28-Nov	99.37		297.47	192.53
Average	97.93	9.81	296.48	189.54
SD	1.64	0.56	7.62	3.51
CV	1.68	5.73	2.57	1.85

* This is multi-day testing over 2 months, as opposed to sample repeats in the same batch in the same day. Variations are expected to be greater.
** All quality control standard results passed a daily +/- 10% validation check
*** Tap water and freshwater concentrations were known to fluctuate over the 2 months.

Hints/Suggestions:

1. Ensure that the electrode is completely filled with solution before each run.

2. Electrodes generally last for six months to one year depending on sample type and frequency of use. Samples that are highly acidic, basic, or abrasive will limit the lifespan of the electrode, as will solvent-based samples. It is highly recommended that customers order a new electrode every six months or when the calibration limits have been exceeded.
3. Purge the buret and prime transfer lines daily.
4. Perform a pH calibration (standards: pH 4, 7, 10 buffer solutions) before every run (if applicable). Calibrations should have a slope of 59 ± 6mV/pH unit at 25ºC, and an intercept that is consistent beginning at 0 ± 100mV for a new electrode. If the electrode calibration consistently falls outside these limits, the electrode has been worn out or over-aged and erratic pH readings may result. The electrode should be discarded, and a new electrode should be used.
5. All sample vessels should be pushed fully into the rack and be level with the bottom of the rack.
6. Ensure the autosampler is placed on a flat level surface.
7. Calibrate IntelliVol™ system every three months, or as required if standard results start to deviate from expected values.
8. When calibrating, make sure there are no deionized water droplets above the level of the water in the vessel as these can increase mass and increase the calibrated volume (mass calibration only).
9. Only use a trusted standard and titrant when calibrating the system

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