Multiparameter Analysis and Enhanced Productivity by the Consolidation of Inorganic Wet Chemistry Methods

Robert V. Menegotto

MANTECH, Guelph, Ontario, N1H 6J2, Canada; rmenegotto@mantech-inc.com; 519-763-4245

Multitasking and time allocations are key components to running an efficient laboratory and decreasing the cost per analysis for pH, conductivity, alkalinity, chloride, fluoride and ammonia. The cost of analysis has risen over the years while revenue from these parameters has remained the same. Much of the high cost is due to the use of multiple instruments, multiple trained technicians and outmoded automation available. By the development of a single automated system, with computer control, capable of connecting multiple electrochemical sensors (e.g., pH, conductivity and Ion Selective Electrodes – ISE's), the research showed that the cost of analysis could be significantly reduced by analysing all these parameters from one sample. Analysis costs were reduced by 80% or more depending upon the actual parameters measured and autosampler size used. Important criteria for the success of these analyses included automatic pipetting, titration capability, delta time/delta mV stability variables, non-linear calibration curves, automatic dilution capability and electronically isolated electrode boards. In addition, it was found that the conductivity probe must be separated from all other electrodes, due to reference electrolyte interference from the pH and ISE electrodes. By employing these techniques, the detection limits for each analyte were not affected. For alkalinity and chloride it was 1ppm, for fluoride less than 0.1ppm, for ammonia less than 0.05ppm and for conductivity, values below 2uS were successfully measured. Statistical results for each parameter measured from a single sample cup, over a large concentration range will be presented. Actual cost savings calculations and method details with correlation to approved methods will also be presented.

Introduction

Multitasking and time allocations are key components to running an efficient laboratory and decreasing the cost per analysis for pH, conductivity, alkalinity, chloride, fluoride and ammonia. As evidenced by a News Release in Ontario, "Harris Government Action Plan to Improve Water Quality Includes Tough New Regulation"[1], both the scope and frequency of testing for these parameters and others continues to increase as governments enact tougher environmental regulations. The cost of analysis has risen over the years while revenue from these parameters has remained unchanged or decreased. To control costs, laboratories in government and industry have instituted hiring freezes, thereby, increasing the workload and responsibility of laboratory chemists. This is not the optimal environment for making informed, confident and legally enforceable analytical decisions. Any automation available for these laboratories would help alleviate the workload and provide increased confidence in data reporting.

For pH, conductivity, alkalinity, chloride, fluoride and ammonia, much of the high cost of analysis is due to the use of multiple instruments, multiple trained technicians and outmoded automation available. These parameters are important since they have well defined standard limits for health and environmental considerations.

This paper describes the development of an automated measurement system for pH, conductivity, alkalinity, chloride, fluoride and ammonia. The experimental results will show that these parameters can be measured in the same system, that approved methods can be followed and that the cost of analysis can be significantly reduced while maintaining confidence in the measurements.

Experimental Design

To be successful in the design of an automated analysis system for pH, conductivity, alkalinity, chloride, fluoride and ammonia, key criteria were set out. The automated system must follow and meet all Environmental Protection Agency (EPA) and Standard Methods for the Examination of Water and Wastewater (SM) published methods. Table 1 provides a reference for all methods discussed in this paper. To decrease the cost per analysis, the system should employ a robotic sampling system with significant sample capacity allowing for large unattended runs. Also, all parameters (pH, conductivity, alkalinity, chloride, fluoride and

Parameter	EPA Method Number[2]	SM Method Number[3]
pH	150.1, 150.2	4500-H+ B
Conductivity	120.1	2510B
Alkalinity	310.1	2320B
Chloride		4500-CL- D
Fluoride	340.2	4500-F- C
Ammonia	350.3	4500-NH3 D

Table 1: List of EPA and SM Approved Methods

Ammonia) should be analysed from the same sample cup. Based on the approved methods (Table 1), a system design capable of pH, conductivity, ion selective electrode (ISE) measurement and calibration, plus titration was required.

For measurement of all parameters from the same sample cup, potential contamination and interference effects on results were considered. Both chemical and electronic requirements were determined and used.

The analysis of alkalinity, chloride, fluoride and ammonia required chemical addition making the analysed sample unsuitable for further testing. For example, after completion of the alkalinity analysis, which requires titration with sulfuric acid, the sample was unsuitable for fluoride analysis. This required the development of an analysis vessel separate from the sample cup. An automatic sample transfer system for pumping the sample from the sample cup to the analysis vessel was therefore used. This ensured that the original sample was not chemically altered in any way, thus suitable for multiple analyses.

By not adding any reagent chemicals to the sample prior to transfer, any required reagent addition must be automated. For example, fluoride analysis requires the addition of total ionic strength adjustment buffer (TISAB) and ammonia analysis requires the addition of 10N sodium hydroxide. These reagents were automatically added to the analysis vessel using reagent addition pumps.

The measurement of conductivity has potential interferences from the presence of other measuring electrodes which use a reference electrode. These reference electrodes will leak salt, normally potassium chloride, into the sample. This leads to a high, inaccurate conductivity result. To eliminate this interference, the conductivity was completely separated from all other measuring electrodes. This was accomplished by having the conductivity measured in the sample cup prior to transferring the sample to the analysis vessel. Temperature compensation for the conductivity was also completed at the time of measurement.

In the analysis vessel, four different measuring electrodes were required to complete these tests. They were a pH electrode, a fluoride ISE, an ammonia ISE and a silver/sulfide ISE (for chloride). When multiple measuring electrodes are used in the same vessel, electrical interference due to multiple ground paths and competing references may occur. These two interfering effects may lead to the formation of ground loop currents between electrodes, which may cause erratic measurements. This electrical interference was eliminated by using a multiple analog electrode device with electronically isolated electrode inputs.

Potential contamination from sample to sample and from method to method was considered. This was eliminated by the adoption of a flexible rinsing system using deionized water. The analysis vessel was drained and rinsed prior to a change in method or sample. The sample transfer tubing and conductivity cell were rinsed prior to a change in sample.

Equipment Used
To satisfy the requirements of the experimental design, a PC-Titrate[TM] System with PC-Titrate software, 2 burets, 2 reagent addition pumps, conductivity meter and MEGA TitraSip[TM] autosampler were used. The equipment was manufactured by Man-Tech Associates, 2 Admiral, Place, Guelph, Ontario, Canada. The electrodes used were a Man-Tech TitraFlo[TM] pH electrode, a Man-Tech fluoride ISE, a Man-Tech silver/sulfide ISE and a Man-Tech ammonia ISE. The pH, fluoride and silver/sulfide electrodes were all combination glass bodied, double junction reference electrodes. The ammonia ISE was an epoxy bodied gas sensing electrode. The conductivity cell had a cell constant of 1.00 and a built-in temperature sensor.

Experimental Approach
A series of standards for each parameter were prepared. The concentration range bracketed typical water samples from low to high concentrations. Each parameter was analysed individually to determine the accuracy and precision without influence from other measurements. Once completed, a multi-parameter standard was analysed. Each parameter was measured in the sample cup before moving on to the next sample. Both blanks and tap water were also analysed in the same manner. After completion of the experiment, the actual cost of analysis was approximated.

Results and Discussion
Table 2 lists the results of the individual measurements. The different concentration ranges for each parameter were randomly placed throughout the rack. All results showed a good distribution around the mean. Figures 1 and 2 show typical statistical charts. In addition, the precision decreased as the concentration of the parameter increased.

Par.	EV	Actual	%Rec[4]	SD	CL[5]
Cond.	blank	2.3	N/A	0.6	0.09
	73	75.9	104.0	1.1	0.10
	717	704.6	98.3	2.7	0.30
	1413	1423.8	100.7	4.7	0.78
	12900	12720.4	98.6	42.2	4.44
Alk.	1.00	1.17	117.0	0.10	0.04
	10.00	10.48	104.8	0.40	0.07
	100.00	105.66	105.7	0.63	0.13
	500.00	510.79	102.2	1.05	0.22
Cl	1.00	0.99	99.0	0.15	0.01
	5.00	5.07	101.4	0.18	0.10
	10.00	10.04	100.4	0.25	0.05
	50.00	50.68	101.4	0.33	0.07
	250	252.26	100.9	0.86	0.19
F	blank	0.004	N/A	0.001	0.001
	0.10	0.11	110.0	0.01	0.004
	0.50	0.53	106.0	0.04	0.02
	1.00	1.11	111.0	0.08	0.02
	10.00	10.22	102.2	0.25	0.14
NH3	blank	0.00	N/A	0.00	0.00
	0.02	0.01	50.0	0.006	0.003
	0.20	0.25	125.0	0.04	0.02
	1.00	1.11	111.0	0.10	0.11
	10.00	10.44	104.4	0.30	0.70

Table 2 : Single Parameter Analysis per Sample (Par.=parameter; EV=expected value; Actual=experimental mean; SD=standard deviation; %Rec=percent recovery; CL =confidence limit with 98% confidence from Student's Variable; Cond.=conductivity, uS; Alk.=alkalinity, ppm; Cl=chloride, ppm; F=fluoride, ppm; NH3=ammonia, ppm, N/A=not available, number of samples analysed, n, varied from 7 to 24)

The conductivity was calibrated with a 1413uS standard. The resulting cell constant from the calibration was 0.98 and this was used in all measurements. The measurements were temperature compensated to 25 degrees Celsius using the built-in temperature probe. The results showed good precision, percent recovery and confidence limits. There was no evidence of carry over in low conductivity samples following a high conductivity sample. The blank value was analysed alone to provide a baseline for the deionized water value. This would then be compared to the value determined in the multiparameter analysis

The pH was calibrated using 4, 7 and 10 pH buffers. This calibration shown in figure 3 was fitted by linear regression. It was used for both initial pH measurement and pH measurements throughout the alkalinity titration. The pH measurements were temperature compensated using a thermistor probe in the analysis vessel. A good pH calibration was important since the alkalinity results were derived from set pH endpoints. The alkalinity results showed good precision, percent recovery and confidence limits. Figure 4 shows a typical alkalinity
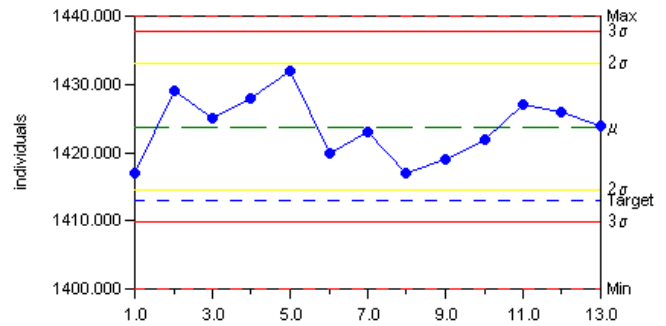

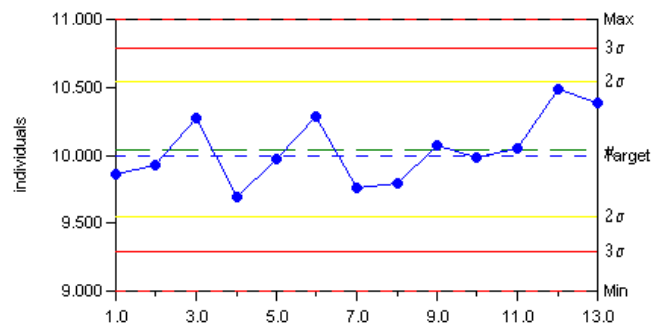**Figure 1: Statistical Chart for 1413uS Conductivity Results**

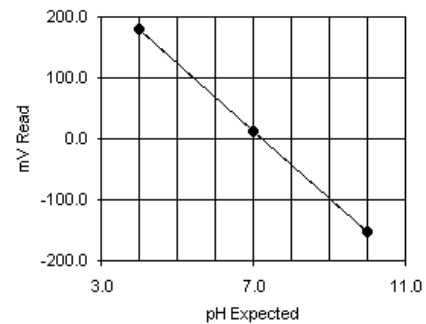**Figure 2: Statistical Chart for 10ppm Chloride Results**
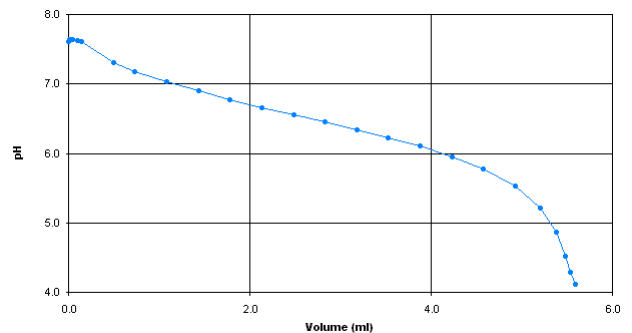

Figure 3: pH Calibration Curve

Figure 4: Alkalinity Titration Curve

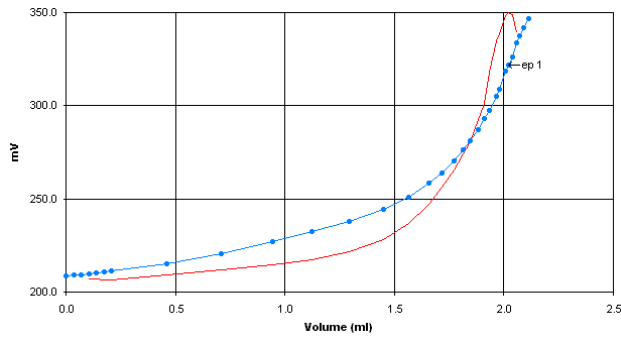**Figure 5: Chloride Titration Curve**

Figure 6: Fluoride Calibration Curve

titration curve. A dynamic injection control was used during the titration. This enabled very low volume injections approaching the endpoint. The 1.00ppm standard gave a method detection limit (MDL) of 0.30. This means that 1.00ppm is a good estimate for the MDL. MDL is determined by the SD multiplied by 3.143 (Student's t value for 7 samples at a 98% confidence level).[6]

The chloride was analyzed by titration with inflection endpoint analysis. The software used a first derivative filter for endpoint detection and the second derivative to determine the exact endpoint mV and volume values. Figure 5 shows a typical chloride titration curve. The chloride results showed good precision, percent recovery and confidence limits. A dynamic injection control was used during the titration. The 1.00ppm standard gave a MDL of 0.48. This is well below the standard value.

The fluoride was analyzed by direct measurement. Figure 6 shows the calibration curve for the fluoride electrode. A point to point logarithmic fit was used since the electrode does not exhibit a linear response over the required measurement range. The stability criterion used was 0.1mV/30 seconds with a maximum of 600 seconds. The 1.00pm percent recovery was high and requires further testing. The 0.10ppm result gives a MDL of 0.03, well below the standard value. Based on this, the fluoride electrode should have a lower detection limit and this is supported by present literature.[7]

The ammonia was analyzed by direct measurement. Figure 7 shows the calibration curve for the ammonia electrode. A point to point logarithmic fit was used since the electrode does not exhibit a linear response over the required measurement range. This particular test has shown measurement stability problems due to the memory the electrode carries over from previous measurements. To help establish a constant
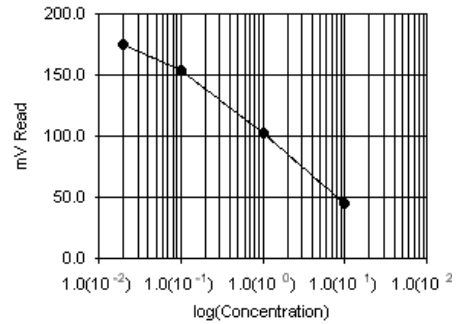
measurement starting point for every sample, a 3 stage rinse was used.[8] The electrode was rinsed with an acid solution, followed by 0.02ppm ammonia standard, followed by deionized water. In addition, the stability criterion of 0.2mV/7seconds for a maximum of 900 seconds ensured stable readings were used for measuring the ammonia concentration. This was successful in that the blank produced a result of 0.00ppm even after a 10.00ppm sample. The percent recoveries and standard deviations for the lower concentrated samples were biased high. This was probably due to the 0.02ppm
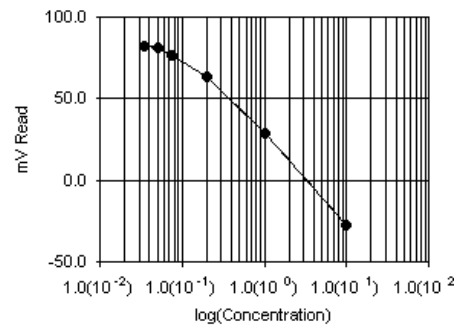

Figure 7: Ammonia Calibration Curve

ammonia rinse solution being depleted during the run. The blank results in Figure 6 also showed a trend upwards towards the end that supports this theory. This supports the stability problem due to memory effects, but it needs to be investigated further. The 0.02ppm result gives a MDL of 0.02, which supports the published detection limit for this method.[8]

Table 3 lists the results of multiple parameter measurements from a single sample. The samples used were blanks, tap water and a multi parameter standard from Environmental Resource Associates (ERA)[9], Lot Number 99103. The statistical charts for the ERA results are shown in figures 8, 9, 10, 11 and 12 since they include acceptance (minimum and maximum) limits suggested by the manufacturer.
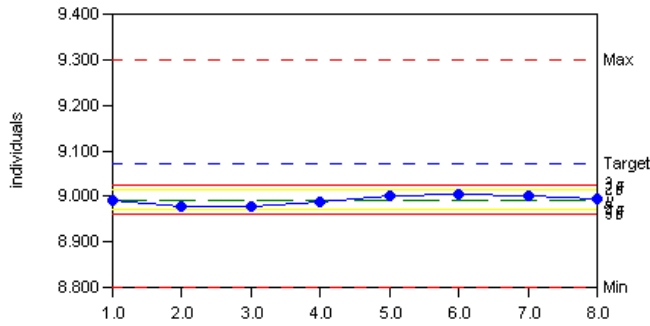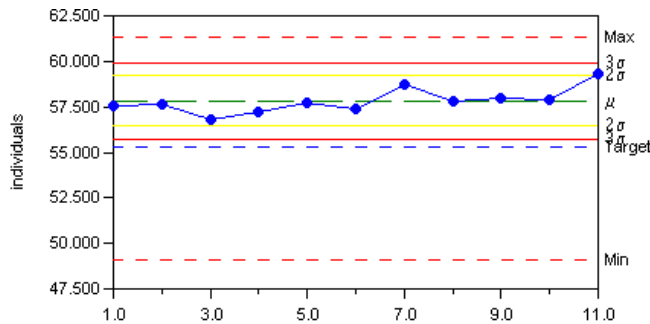
Figure 8: ERA pH Results

Figure 11: ERA Fluoride Results

Figure 9: ERA Alkalinity Results

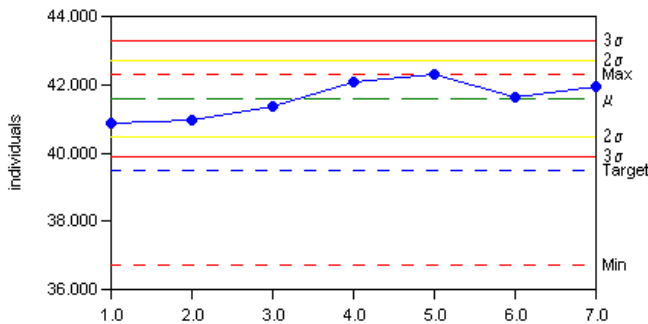**Figure 12: ERA Conductivity Results**

Figure 10: ERA Chloride Results

Ammonia was excluded from this since it was not a parameter available with the multi parameter standard.

Also, in a real laboratory setting, many ammonia samples are preserved in an acid medium, therefore, it could not be analyzed with these parameters. If required in an unpreserved sample, it is theorised that ammonia may be analyzed from the same sample, but further research is required.
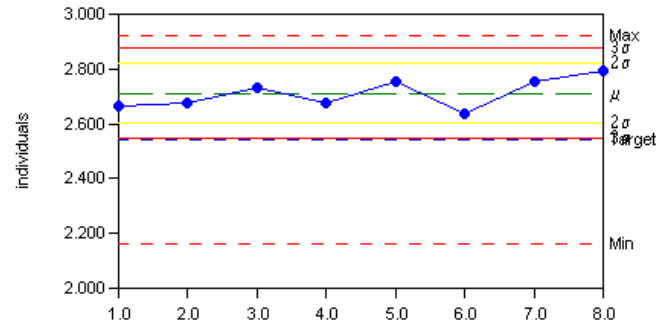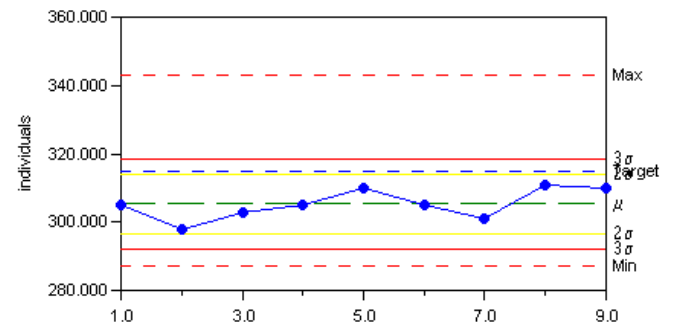
The actual sequence of analysis for conductivity, pH, alkalinity, chloride and fluoride was:

1. Measure conductivity in the sample.
2. Transfer 20mL to analysis vessel.
3. Measure pH and titrate for alkalinity.
4. In the same aliquot titrate for chloride.
5. Drain the sample, rinse and drain.
6. Transfer 10mL of sample plus 10mL of TISAB.
7. Measure for fluoride.
8. Drain, rinse and drain.
9. Repeat steps 1 to 8 for the next sample

For chloride, the initial analyses showed a high bias in the results, including the blank. For example, the blank produced a result of between 5 to 6ppm. These results forced us to look at the system configuration and electrodes. We pinpointed the potassium chloride (KCl) fill solution in the pH electrode. Since the pH electrode has a high reference flow for quick response, and stable measurement in low ionic strength samples, the KCl leaked into and contaminated the sample. This was confirmed by removing the pH electrode for a duplicate set of chloride analyses. The chloride results decreased or were zero for the blank. We eliminated the chloride from the electrode by switching to a high flow pH electrode with potassium nitrate fill solution.

Par.	EV	Actual	%Rec[10]	SD	CL[11]
Blank					
Cond	N/A	2.1	N/A	0.96	0.43
pH	N/A	6.00	N/A	0.26	0.12
Alk	N/A	0.68	N/A	0.48	0.22
Cl	N/A	0.00	N/A	0.00	0.00
F	N/A	0.008	N/A	0.002	0.00
Tap Water					
Cond	N/A	755.4	N/A	11.62	5.22
pH	N/A	7.67	N/A	0.08	0.04
Alk	N/A	273.79	N/A	1.90	0.85
Cl	N/A	42.09	N/A	0.55	0.25
F	N/A	0.34	N/A	0.02	0.01
ERA 99103					
Cond	315	305.3	96.9	4.39	1.41
pH	9.07	8.99	99.1	0.01	0.00
Alk	55.3	57.83	104.6	0.69	0.26
Cl	39.5	41.59	105.3	0.56	0.21
F	2.54	2.71	106.7	0.06	0.02

Table 3: Multi-parameter Analysis from a Single Sample (n = 7 samples for the blank and Tap Water and 8 for the ERA standard)

The results for multi parameter analysis were the same or better than that shown when each analyte was analyzed separately. The correlation with a known standard is very good. Also, the conductivity blank values showed excellent correlation to those analyzed singly (Table 1). This is evidence that there was no carry over, cross contamination or interfering effects.

A series of duplicates were also analysed with the blank, tap water and multi parameter samples. Table 4 shows the Relative Percent Difference (RPD) for parameter. Normally laboratories accept RPD's between 10-20% for their quality control protocol. Except for the blanks, the results were significantly less than this. The blanks will tend to be higher since measurements are normally less than or equal to the detection limits. For this reason, blanks are normally not used for RPD analysis.

Dup.	Relative Percent Difference				
	Cond.	**pH**	**Alk.**	**Cl**	**F**
Blank	42.0	3.87	34.7	0.0	57
TW1	0.1	0.3	0.2	1.9	1.3
TW2	1.8	0.0	0.4	3.0	0
ERA1	0.7	0.0	0.6	7.8	1.0
ERA2	0.3	0.1	2.5	1.5	0.8

Table 4: Relative Percent Difference Duplicate Analysis (Dup. = Duplicate; W = Tap Water)

This entire analysis procedure (samples, pipetting. duplicates, rinsing, etc.) was completely automated. By analysing all the parameters from a single sample cup with the same system, there were no apparent negative effects on the result. To the contrary, they may have improved. A definite improvement was evident with fluoride results. This may have been due to the calibration curve developed from the single fluoride analysis. The standards were freshly prepared for this multi parameter analysis and the calibration curve improved which likely improved the fluoride results.

In general, the single parameter and multi parameter results were good and comparable to those shown in the EPA[2] and Standard Methods[3]. Compared to manual analysis or even outmoded technology, the results may improve. The reason is samples are analyzed in identical fashion each time, therefore, there is no human operator variability.

Cost of Analysis

The actual cost of analysis will vary from laboratory to laboratory. Table 5 and Figure 13, however, show a set of estimated costs which may be compared by laboratories to their actual costs. The cost per sample is calculated using the following formula:

Cost per Sample = Total Cost per Day/Samples per Day

As can be seen from this table, the cost of analysis, compared to outmoded systems, or lack of equipment, is reduced considerably. This is due to the elimination of manual pipetting and running all parameters from a single sample cup. Other savings include decreased turnaround time, decreased sample handling and decreased operator training. In addition, the automated system increases the laboratory's performance by increasing the confidence in the results obtained.

Item	Outmoded Systems	Multi parameter System
Technician Time/day	4.0 hours = $100.00	0.42 hours = $10.50
Supplies/day	$15.00	$12.00
Overhead/day	$57.50	$11.25
Cost per sample for 5 parameters	**$13.26**	**$2.60**

Table 5 : Cost of Analysis Comparison for Conductivity, pH, Alkalinty, Chloride and Fluoride; the following estimates were made, 3250 samples/year, 13 samples/day (250 working days in a year), $25.00/hour labor rate, and a 50% overhead rate
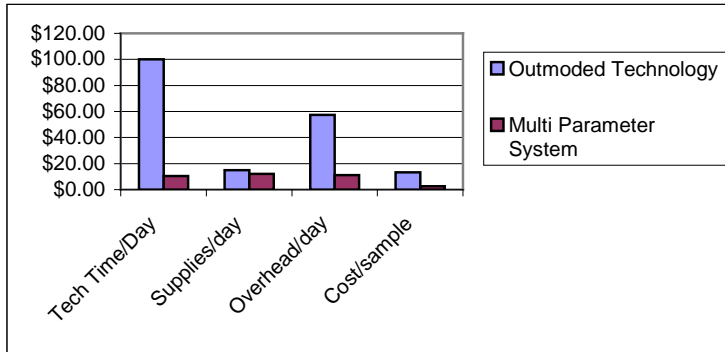
Figure 13: Cost per Sample Comparison Chart

Conclusion

An automated system to determine conductivity, pH, alkalinity, chloride and fluoride from a single sample is possible. The cost of analysis is significantly reduced and there is increased confidence in the results due to the minimisation of operator intervention allowing samples to be analysed in a consistent manner. Further research into detection limits and combining ammonia should be completed.

[1] Office of the Premier, News Release, Government of Ontario, August 8, 2000

[2] Methods for Chemical Analysis of Water and Wastes, Environmental Protection Agency
http://www.epa.gov/OGWDW/methods/inch_tbl.html;
http://www.epa.gov/OGWDW/methods/2nd_tbl.html;

[3] Standards Methods for the Examination of Water and Wastewater 23rd Edition, American Water Works Association

[4] Environmental Sampling and Analysis Lab Manual, Maria Csuros, 1997 CRC Press, pp. 33

[5] Environmental Sampling and Analysis Lab Manual, Maria Csuros, 1997 CRC Press, pp. 34-35

[6] Environmental Sampling and Analysis Lab Manual, Maria Csuros, 1997 CRC Press, pp. 32

[7] Application Note 031, Fluoride by Direct Measurement, MANTECH, www.mantech-inc.com

[8] Application Note 050W, Ammonia by Direct Measurement 0.02-100ppm, MANTECH, www.mantech-inc.com

[9] Environmental Resource Associates, 5540 Marshall Street, Arvada, CO, 80002

[10] Environmental Sampling and Analysis Lab Manual, Maria Csuros, 1997 CRC Press, pp. 33

[11] Environmental Sampling and Analysis Lab Manual, Maria Csuros, 1997 CRC Press, pp. 34-35