CATION CONDUCTIVITY TEMPERATURE COMPENSATION

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SUMMARY: Cation conductivity is one of the most important on-line cycle chemistry measurements in today's power plant. It is relatively simple, sensitive, low cost and reliable. But is it accurate? Often taken for granted, cation conductivity accuracy depends heavily on the sample temperature variability and the temperature compensation algorithm used.   The cation conductivity temperature compensation performance of current instrumentation has been examined over a wide range of conductivity and temperature and compared with new developments. Surprisingly large errors have been found.

INTRODUCTION

The importance of temperature compensation of high purity water conductivity measurements has been widely recognized in the power industry. The development of microprocessor-based conductivity instrumentation in the 1980s brought with it the first commercially available equipment to provide reasonable temperature compensation accuracy. It also initiated concern about the algorithms used. At the same time, the first EPRI (Electric Power Research Institute) guidelines for cycle water chemistry were published, setting specific and cation conductivity limits for various points in the cycle. Maintaining absolute values rather than just monitoring trends for upsets was seen as vital to long term corrosion and deposition reduction. The high and variable conductivity temperature coefficients, the wide variation of many sample temperature controls and the vulnerability of sample temperature to ambient changes downstream of temperature controls justify real concern over the type of compensation provided.

More than a decade later, little of available high purity conductivity instrumentation has changed despite improvements in microprocessor memory and computational methods. There is also greater reliance on cation conductivity as the key water chemistry parameter, particularly with oxygenated treatment. Presented here is a background of conductivity temperature compensation evolution in the power industry, a recent evaluation of cation compensation methods in use and a comparison with new developments.

BACKGROUND

Conductivity is primarily used as a measure of ionic concentration. However, conductivity is also sensitive to temperature. Nearly all conductivity measurements and specifications are therefore referenced or compensated to a fixed temperature, usually 25°C, in order to refer to a specific level of contamination. That is, the conductivity is readout as if the temperature of the sample were at 25°C, regardless of the actual

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measurement temperature. The methods to provide this temperature compensation vary widely in the level of complexity and accuracy, as this work will demonstrate.

Close temperature control of samples in the sample line is a good, though expensive, practice. It minimizes secondary effects of temperature such as high temperature reactions, varying attraction of trace ions to built-up solids on the sample line wall and ambiguities of compensation when the composition of the sample differs significantly from that for which temperature compensation algorithms are intended. However, temperature control is not a complete substitute for temperature compensation since controls do fail and develop wide tolerances and samples are influenced by ambient conditions in the lines between the cooler and the sensors.

HIGH CONDUCTIVITY TEMPERATURE COMPENSATION

The temperature coefficients of most neutral salt ionic contaminants in water are approximately linear, near 2% of conductivity value per °C. This has allowed instrumentation for general purpose conductivity measurements to use very simple temperature compensation methods. It should be noted that most portable and laboratory conductivity instrumentation still uses this limited type of compensation.

Acids and bases have somewhat lower temperature coefficients, on the order of 1.6-1.9% per °C. This is because of the higher but less temperature-sensitive conductivity of hydrogen (hydronium) and hydroxide ions. Some conductivity instrumentation has the ability to set in a linear temperature coefficient but depends on the user to determine the appropriate value to enter. For acid/base measurements in the percent concentration range (such as used for demineralizer regeneration) some instruments have carefully matched non-linear temperature compensation

algorithms as well as precise non-linear conductivity to concentration conversion for specific acids and caustic. These extensive algorithms can be activated by simple menu selection.

Other instruments require the user to enter a matrix of conductivity to concentration data plus an appropriate temperature coefficient in order to achieve direct concentration readout. Users should be aware of this requirement since the data is often not available and typically requires extensive laboratory work to obtain. The resulting temperature compensation may have limited range or limited accuracy since many percent concentration samples have non-linear temperature characteristics.

LOW CONDUCTIVITY TEMPERATURE COMPENSATION

Pure waters present a different challenge to appropriate temperature compensation. With most materials, the ion concentration remains relatively constant with temperature. The temperature effect is largely due to the improved ionic mobility at higher temperature, which in turn is due to the decreasing viscosity of water. For this reason, most salts in water have about the same temperature coefficient, near 2%/°C.

In pure waters, the hydrogen and hydroxide ions from the dissociation of the water itself dominate the conductivity. As the temperature of water increases, the degree of dissociation rises dramatically. The hydrogen and hydroxide ion concentrations increase nearly 22-fold over the range of 0 to 100°C. This causes a much higher and more non-linear conductivity vs. temperature relationship. At 25°C the slope or sensitivity is approximately 5% per °C for pure water and at low temperatures is over 7% per °C. See Figure 1. The properties of pure water conductivity with temperature have been repeatedly examined, resulting in improved accuracy.[1-6]

The compensation for these properties has also evolved and improved. High purity water compensation has traditionally been recognized to consist of two separate components: the properties of the solvent, pure water, and the properties of the solute, the salts in the water. This is appropriate for neutral salt impurities since the ionization of water is influenced only by temperature, not by trace concentrations of salts. Similarly, the mobility and conductivity of trace salt ions varies with temperature, independent of the ionization of water.

The combination of these independent temperature effects was codified decades ago by General Electric for use with measurements on boiling water reactor (BWR) samples. This was the so-called G.E. equation, Eq. (1). Note specific parts of the equation: C_w and 0.0545 describe the properties of pure water and 0.02 represents the typical 2%/C temperature coefficient of neutral salts. There is a direct correlation between water's physical properties and the parts of the equation describing the compensation.

$$C_{25°C} = \frac{C_T - C_w}{1 + 0.02\,(T - 25)} + 0.0545 \qquad (1)$$

C_T = total conductivity at temperature (raw or uncompensated)
C_w = conductivity of pure water at Temperature
T = sample temperature (°C)
$C_{25°C}$ = conductivity compensated to 25°C

The original expression for C_w in the GE equation was an empirical curve match, Eq. (2), which could be calculated fairly easily with a slide rule.[7]

$$C_w = (0.0545)\,(0.55\,e^{\,0.0363\,(T)} - 0.356) \qquad (2)$$

The performance of compensation has been improved both by more accurate knowledge of water conductivity/temperature characteristics and by closer mathematical curve matching to those characteristics over wider temperature ranges. The present state of the art for neutral salt compensation is the G.E.-type equation using the most recent Thornton/Light expressions for C_w and replacing the 0.02 linear coefficient with a more accurate non-linear expression.[6] However, some high purity instruments have not kept up with these more recent developments.

All of the above developments based on separate solvent and solute effects in G.E.-type equations are appropriate only for BWR samples and polished makeup water, where neutral salts are typically the major contaminants. Most other specific conductivity samples will have ammonia or amines dominating the conductivity. Cation conductivity samples have had their cations replaced by hydrogen ion and thus have become acidic solutions. Since these samples are bases or acids rather than neutral salts, a different situation exists. The hydroxide ion of the base and the hydrogen ion of the acid have a direct impact on the ionization of water which also produces these ions. The additional hydroxide or hydrogen ions tend to suppress the ionization of the water itself.

This interaction and its variation with temperature require an entirely different approach to temperature compensation since the solute and water effects cannot be separated. It is not correct as sometimes proposed that the G.E.-type equation can be modified by putting in a different linear coefficient for ammonia or cation conductivity samples. Such an approach does not take into account that the ionization of water has been greatly influenced by the presence of the bases or acids in these samples and therefore the C_w term is no longer applicable. This fact was pointed out some years ago but as not heeded in the development of some instrumentation.[8]

It is fairly straightforward to calculate the conductivity of a solution of known acid or base concentration at various temperatures (see appendix). However, it is not straightforward to compensate those values back to the reference conductivity at 25°C: the difficult job a conductivity instrument must accomplish. For this reason, advanced temperature compensation algorithms have been kept proprietary, buried in microprocessor software. Their performance, however, can be readily assessed.

TEMPERATURE COMPENSATION EVALUATION

Standard high purity neutral salt compensation methods using various modified G.E.-type equations give fairly comparable results. Only the most demanding semiconductor ultrapure water applications require the slightly higher accuracy provided by the most recent work in that area.[6] However, with cation compensation, it was suspected that accuracy with various instruments would vary widely because of the prevalence of false assumptions, limited mathematical capabilities and perhaps some complacency. It was decided to evaluate the cation temperature compensation performance while eliminating other possible sources of error such as cell constant, temperature measurement, cable and cell capacitance, sample contamination, etc., since these are often installation-dependent. A sampling of instruments that provide cation compensation for power plant applications was evaluated. They represent the variety of equipment installed in U.S. power plants today.

As a basis for the evaluation, a table of reference values was established, based on various low concentrations of hydrochloric acid in pure water. Hydrochloric and sulfuric acids have been the most commonly used equivalent for cation conductivity.[9] Their conductivity vs. temperature properties are similar to each other and to many other acids that could be present.

The best available data were used for the ion product of water, the equivalent ionic conductances of hydrogen, hydroxide and chloride ions, plus the density of water, all varying over temperature.[6] These were used in standard physical chemistry equations (see appendix) to obtain the reference values of conductivity vs. temperature at various concentrations of hydrochloric acid which represented particular conductivity values at 25°C.

Simulated uncompensated conductivity signals (resistances) for the full range of temperatures were determined from the reference values above and connected to the input of several manufacturers' instruments. Resistances were made compatible with the appropriate cell constant for each instruments' range. Instruments were made to display precise corresponding temperatures by adjusting the temperature input resistance as needed. The resulting readout of compensated conductivity was tabulated over the range of hydrochloric acid concentrations and over a wide temperature range. These results were then compared with the reference values at 25°C for the corresponding HCl concentration to identify the errors. Results are shown in Figures 2-7 and Tables 2 and 3.

Readily apparent is the variation in accuracy among instruments due to widely varying approaches to the difficult challenge of cation temperature compensation. Instrument A's method apparently attempted to match most closely at 0, 25 and 50 °C points as shown in Figure 2. Instrument B gave a fairly good match from 0-40°C but deviated widely above that, in Figure 3. Instrument C did not have a true cation compensation algorithm but did allow changing the linear temperature coefficient in its G.E.-type equation. No instructions were provided for an appropriate coefficient and attempts at using estimated values gave large errors, examples of which are shown in Figure 4. Some improvement might be possible with more

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information. Instrument D, Figure 5, appeared to match the acid characteristics at high concentration and might be suitable for makeup water treatment cation exchange monitoring. However, for cycle chemistry measurement it is clearly unacceptable.

A more recent unique three-dimensional curve fitting matrix algorithm was developed by Thornton Associates for its instrumentation. Its performance in instrument E is illustrated in Figure 6. A comparison with the other figures makes it clear there has been significant progress toward more accurate cation conductivity temperature compensation. Further comparison is provided with part of the data (simulated pure water and 0.1 µS/cm cation conductivity) listed in Tables 2 and 3 and plotted in Figures 7 and 8. This latest method improves the accuracy of cation compensation by well over an order of magnitude.

CONCLUSION

Wherever cation conductivity measurement is needed, accuracy requirements should consider: 1) the realistic anticipated temperature and conductivity ranges of the sample, 2) the acceptable magnitude of error in cation conductivity measurement and 3) the effective compensation accuracy of the instrumentation over the sample conditions. Careful questioning about the instrumentation and actual evaluation may be necessary since virtually all published accuracy specifications are of the direct conductance measurement capability. Cation compensation performance over temperature and conductivity ranges is never specified.

This work identifies significant errors in widely accepted equipment for this measurement. There is clearly more work needed to evaluate all cation and specific conductivity temperature compensation methods, preferably in an independent investigation. At the same time there is the need for some instrument manufacturers to develop major improvements to their algorithms.

ACKNOWLEDGMENTS

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APPENDIX

Standard values for comparison of conductivity were calculated from the following equations across the temperature range:

$$C = \{ \lambda_{H+} [H^+] + \lambda_{OH^-} [OH^-] + \lambda_{Cl^-} [Cl^-] \} d$$

$$[H^+] = [OH^-] + [Cl^-]$$

$$K_W = [H^+] [OH^-]$$

where
C = total conductivity at temperature
λ_i = respective equivalent ionic conductance at temperature
$[\ ]$ = respective ion concentration
d = density of water at temperature
K_W = ion product of water at temperature

Table 1
Instrument Temperature Compensation Methods

Temp. Compensation Method	Availability	Applications
Fixed 2%/C coefficient	Common with general purpose analog and portable meters.	Cooling towers, wastewater, manufacturing rinse waters, etc… where modest accuracy is acceptable
Adjustable linear coefficient	Many on-line microprocessor-based instruments	Processes where temperature coefficients are known and temperature range is limited
Preprogrammed direct % concentration readout with non-linear compensation	Many on-line microprocessor-based instruments	Deionizer regeneration acids and bases
Matrix % concentration readout with linear coefficient	Some on-line microprocessor-based instruments	Process solutions where extensive concentration vs. conductivity and temperature data are available
High purity water with neutral salts	Some on-line microprocessor-based instruments	Pure makeup water, BWR cycle samples
Cation conductivity/ammonia/ ETA (ethanolamine)	Some on-line microprocessor-based instruments	Cation and degassed cation conductivity samples, ammonia and ETA treated samples

Table 2
Instruments A,B,C, D, & E Cation Temperature Compensation Data for Pure Water

Temp (°C)	Instrument A		Instrument B		Instrument C		Instrument D		Instrument E	
	Comp Cond (μS/cm)	Error (%)	Comp Cond (μS/cm)	Error (%)	Comp Cond (μS/cm)	Error (%)	Comp Cond (μS/cm)	Error (%)	Comp Cond (μS/cm)	Error (%)
0	0.053	-3.7	0.055	-0.1			0.062	13	0.05514	0.2
5	0.043	-22	0.055	-0.1			0.063	14	0.05514	0.2
10	0.043	-22	0.054	-1.9	0.08	45	0.065	18	0.05511	0.1
15	0.045	-18	0.055	-0.1	0.05	-9.2	0.068	24	0.05513	0.1
20	0.049	-11	0.055	-0.1	0.06	9.0	0.076	38	0.05509	0.1
25	0.055	-0.1	0.055	-0.1	0.064	16	0.080	45	0.05517	0.2
30	0.049	-11	0.055	-0.1	0.05	-9.2	0.089	62	0.05507	0.0
35	0.046	-16	0.056	1.7	0.06	9.0	0.099	80	0.05505	0.0
40	0.046	-16	0.056	1.7	0.06	9.0	0.110	100	0.05513	0.1
45	0.052	-5.5	0.057	3.5	0.07	27	0.121	120	0.05500	-0.1
50	0.059	7.2	0.058	5.3	0.08	45	0.138	151	0.05514	0.2
55	0.050	-9.2	0.059	7.2	0.08	45	0.156	184	0.05496	-0.2
60	0.048	-13	0.060	9.0	0.09	64	0.175	218	0.05483	-0.4
65	0.049	-11	0.062	13	0.10	82	0.200	263	0.05486	-0.4
70	0.060	9.0	0.062	13	0.11	100	0.220	300	0.05535	0.5
75	0.069	25	0.064	16	0.12	118	0.253	360	0.05531	0.5
80	0.059	7.2	0.066	20			0.280	409	0.05515	0.2
85	0.052	-5.5	0.067	22			0.308	459	0.05534	0.5
90	0.054	-1.9	0.069	25			0.342	520	0.05509	0.1
95	0.045	-18	0.071	29			0.377	585	0.05538	0.6
100	0.085	54	0.076	38			0.419	661	0.05509	0.1

Table 3
Instruments A,B,C, D, & E Cation Temperature Compensation Data at 0.100 μS/cm

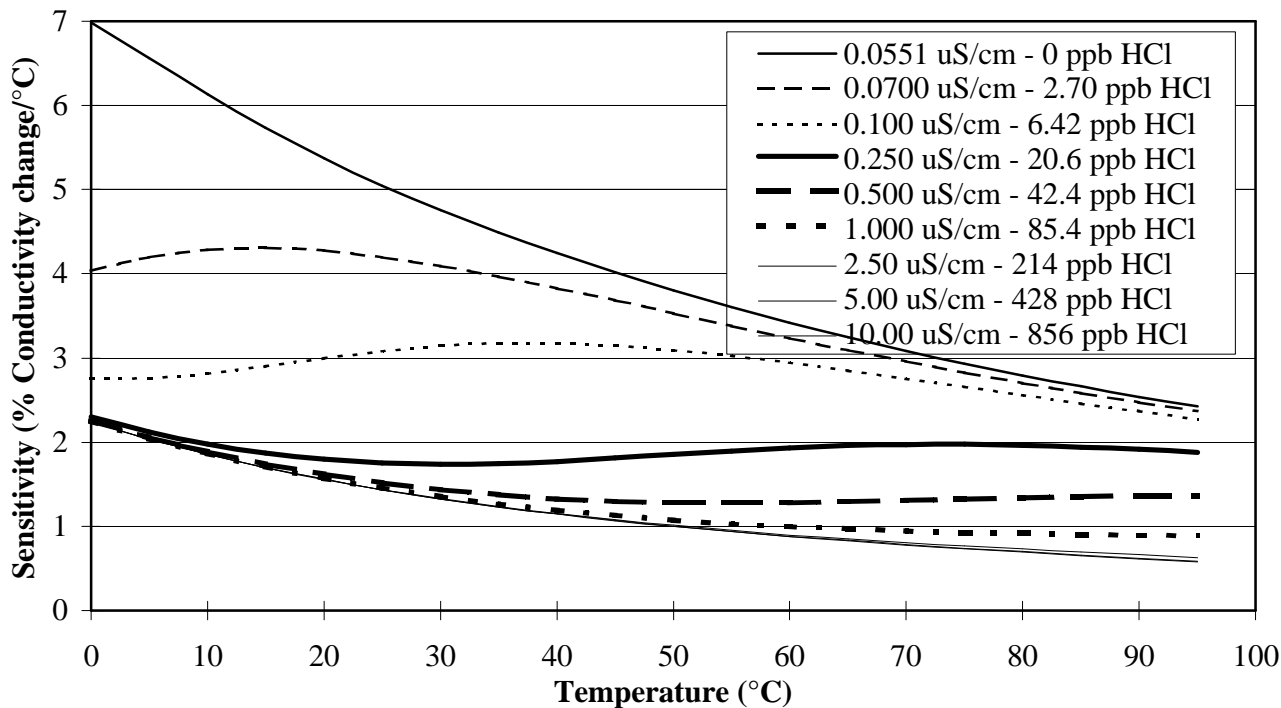| Temp (°C)	Instrument A		Instrument B		Instrument C		Instrument D		Instrument E	
	Comp Cond (μS/cm)	Error (%)	Comp Cond (μS/cm)	Error (%)	Comp Cond (μS/cm)	Error (%)	Comp Cond (μS/cm)	Error (%)	Comp Cond (μS/cm)	Error (%)
0	0.099	-1.0	0.100	0.0			0.098	-2.0	0.0998	-0.2
5	0.096	-4.0	0.101	1.0			0.100	0.0	0.0998	-0.2
10	0.094	-6.0	0.101	1.0	0.200	100	0.101	1.0	0.0999	-0.1
15	0.094	-6.0	0.101	1.0	0.140	40	0.108	8.0	0.0999	-0.1
20	0.096	-4.0	0.101	1.0	0.110	10	0.110	10	0.0999	-0.1
25	0.101	1.0	0.100	0.0	0.101	1.2	0.118	18	0.0998	-0.2
30	0.094	-6.0	0.100	0.0	0.090	-10	0.121	21	0.0997	-0.3
35	0.090	-10	0.099	-1.0	0.090	-10	0.129	29	0.0998	-0.2
40	0.090	-10	0.099	-1.0	0.090	-10	0.139	39	0.0997	-0.3
45	0.094	-6.0	0.099	-1.0	0.090	-10	0.155	55	0.0998	-0.2
50	0.102	2.0	0.105	5.0	0.100	0.0	0.166	66	0.0998	-0.2
55	0.094	-6.0	0.101	1.0	0.100	0.0	0.183	83	0.0996	-0.4
60	0.092	-8.0	0.103	3.0	0.110	10	0.201	101	0.0995	-0.5
65	0.095	-5.0	0.103	3.0	0.110	10	0.220	120	0.1002	0.2
70	0.103	3.0	0.105	5.0	0.130	30	0.245	145	0.1002	0.2
75	0.114	14	0.108	8.0	0.140	40	0.272	172	0.1002	0.2
80	0.106	6.0	0.109	9.0			0.299	199	0.1001	0.1
85	0.102	2.0	0.111	11			0.333	233	0.0997	-0.3
90	0.105	5.0	0.114	14			0.367	267	0.1000	0.0
95	0.131	31	0.115	15			0.402	302	0.0996	-0.4
100	0.128	28	0.122	22			0.438	338	0.1003	0.3

Figure 1
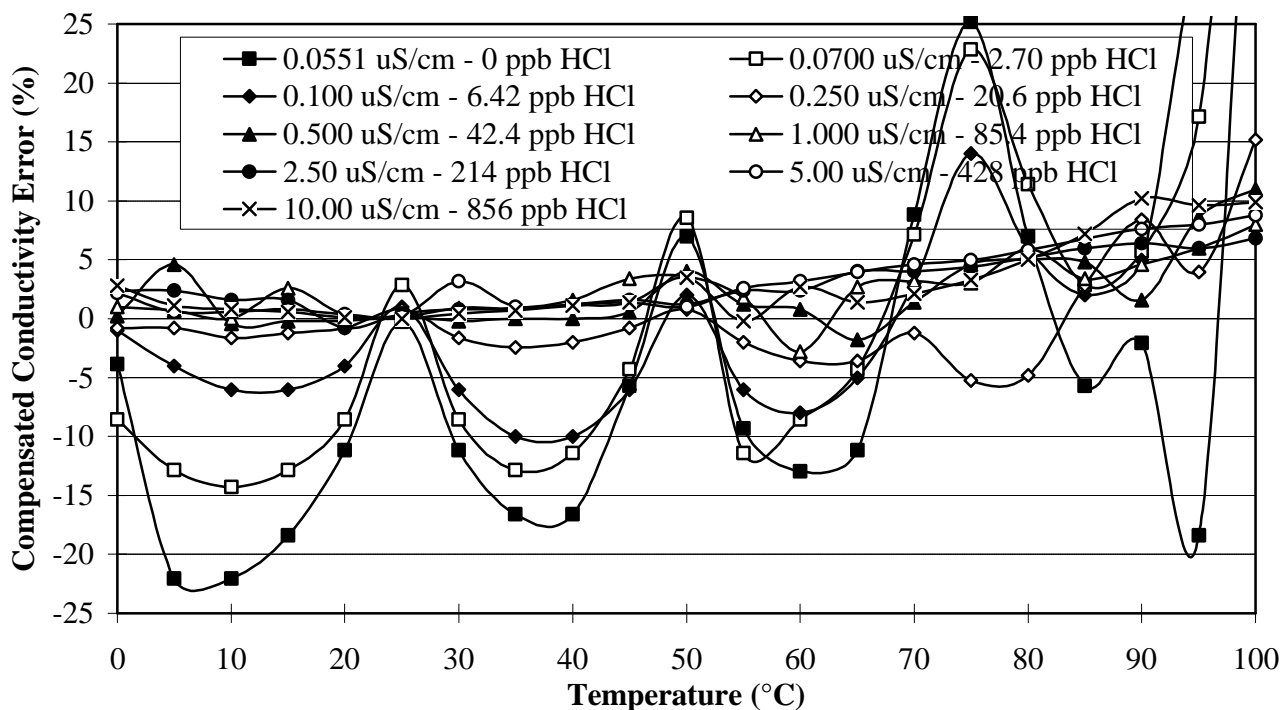**Sensitivity of Cation Conductivity to Temperature**

Figure 2
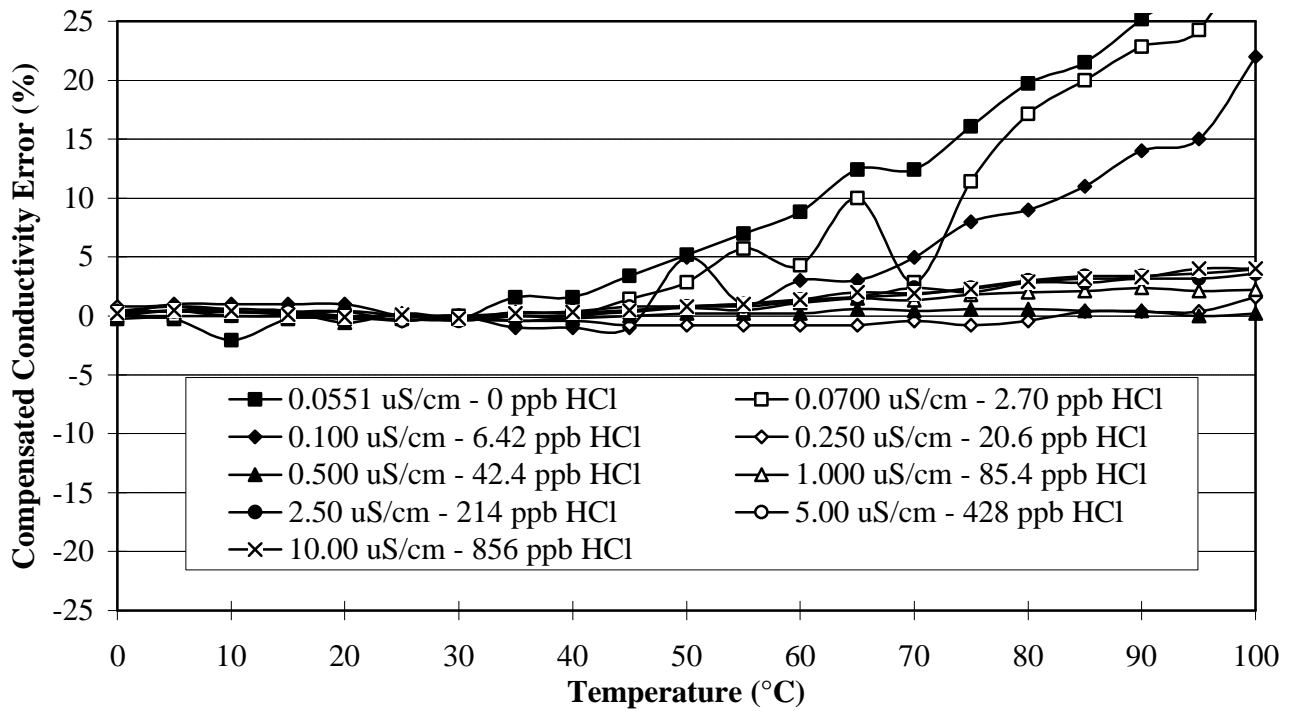**Instrument A Cation Conductivity Temperature Compensation Performance**

Figure 3
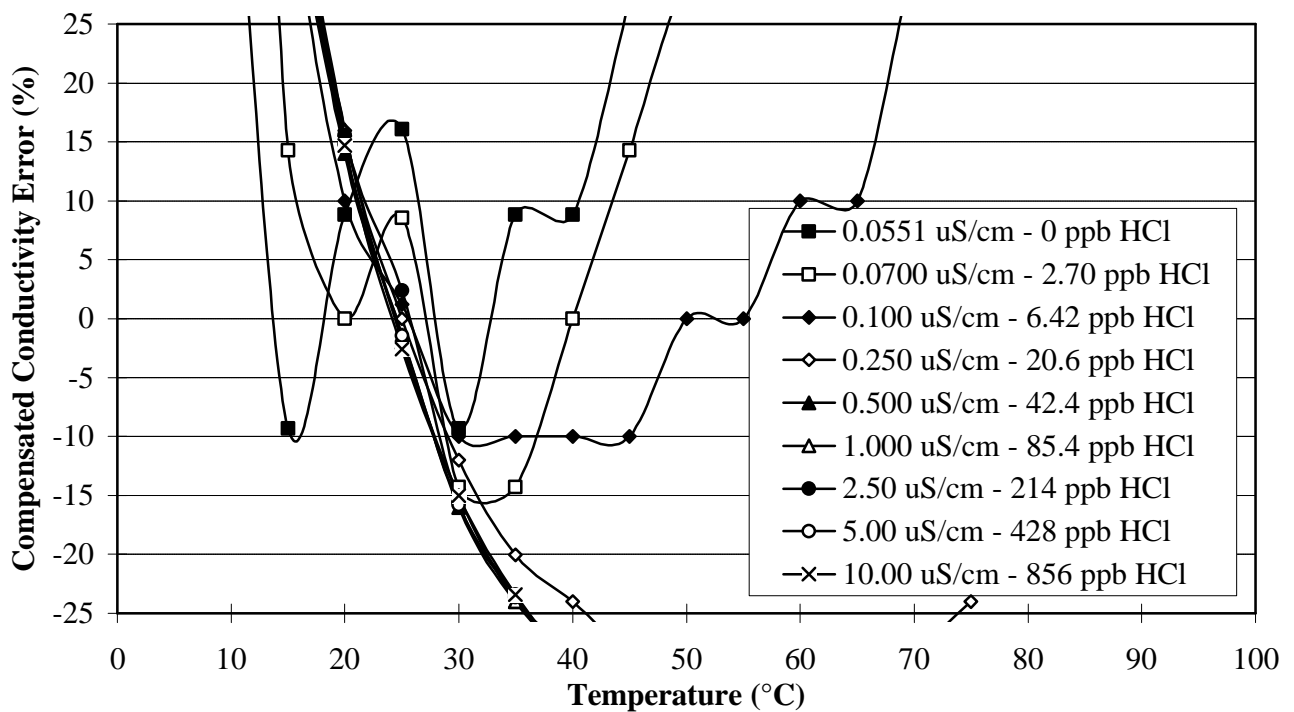**Instrument B Cation Conductivity Temperature Compensation Performance**

Figure 4
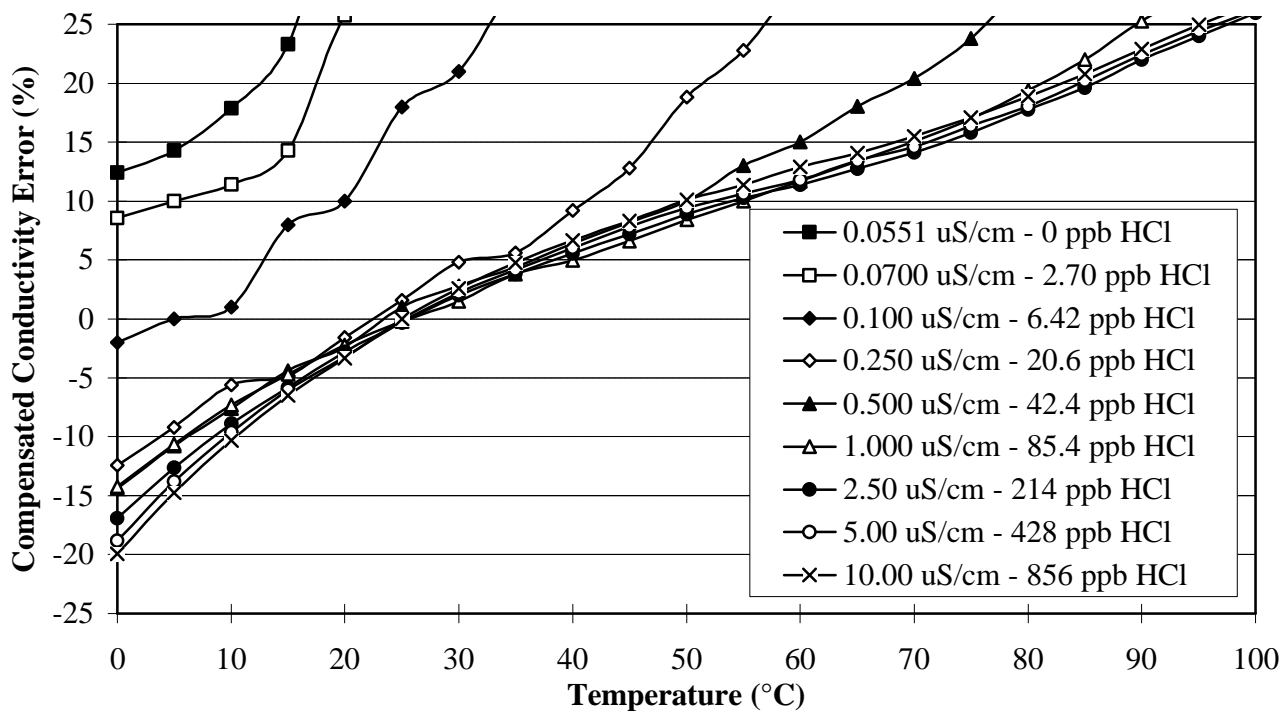**Instrument C Cation Conductivity Temperature Compensation Performance**

Figure 5
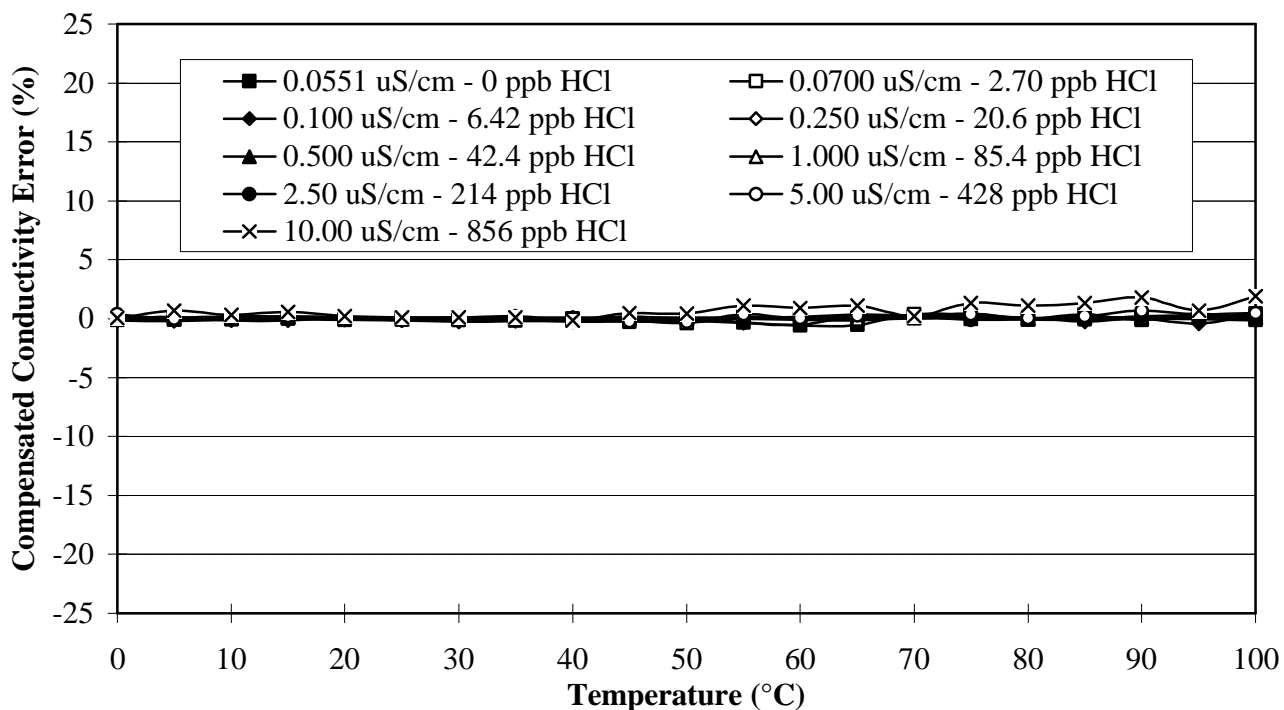**Instrument D Cation Conductivity Temperature Compensation Performance**

Figure 6
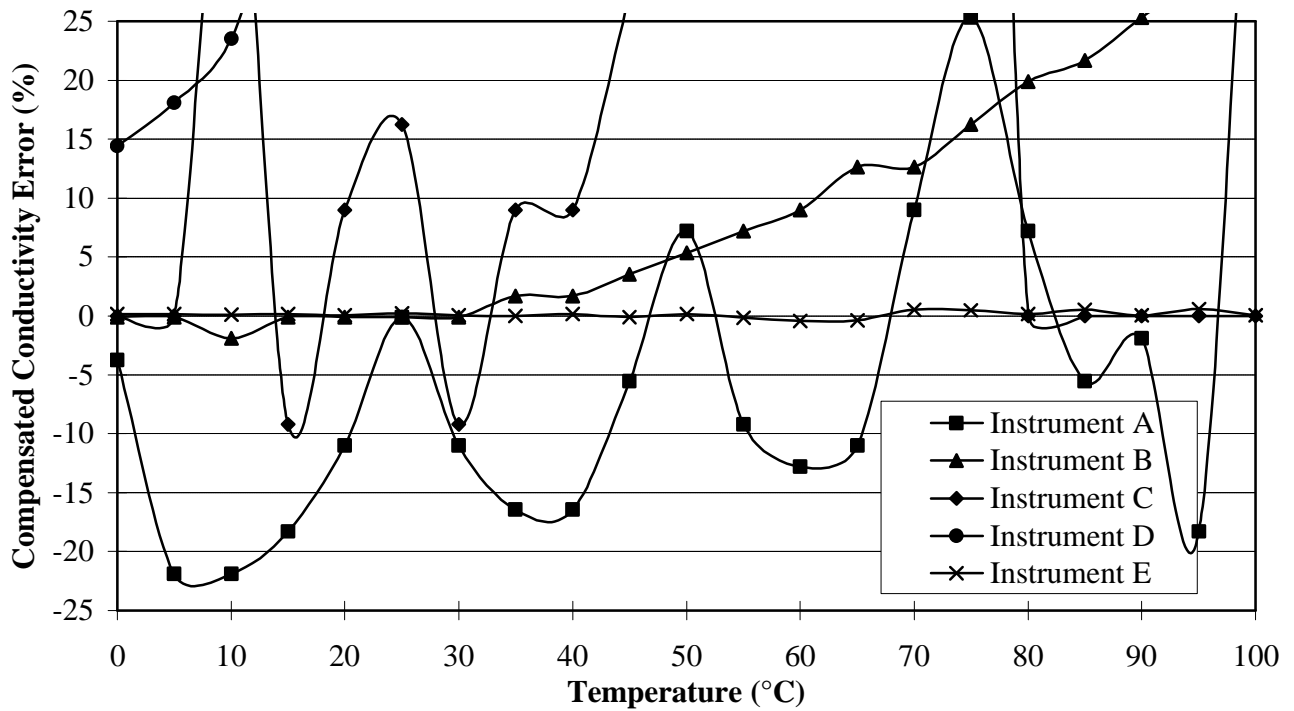**Instrument E Cation Conductivity Temperature Compensation Performance**

Figure 7
Cation Conductivity Temperature Compensation Performance for Pure Water
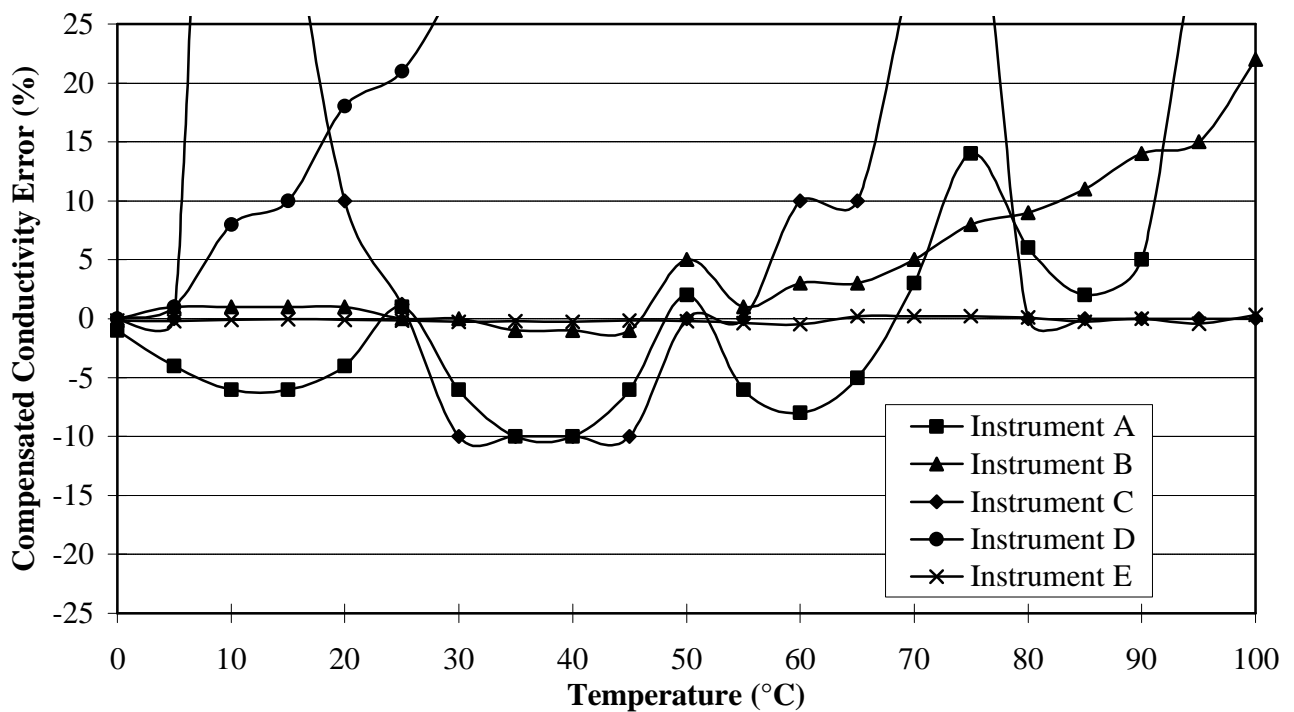

Figure 8
Cation Conductivity Temperature Compensation Performance at 0.1 µS/cm