Proceedings World Geothermal Congress 2015
Melbourne, Australia, 19-25 April 2015

Steam Purity Monitoring of Low Sodium by Ion Selective Electrode Method

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Keywords: DIPA (Di-Isopropylamine), 808 Titrando, Atomic Absorption Spectrophotometer, Ionic Strength adjustor, ISE (Ion Selective Electrode), NH_4Cl/NH_4OH, ROSS Sodium electrode

ABSTRACT

The steam supplied to steam turbines in geothermal power plants contains impurities such as silica and chloride ions, as well as gases which cause scales to stick to the turbine blades or reduce the vacuum in a condenser. To accurately control the plant water (steam) quality, online measurements of both steam water quality and gas volume are taken. Sodium in steam is an indication of brine carry-overs, so this is monitored in the power plant to measure steam purity. The current system of on-line monitoring of sodium employs the flame photometry method. From 1998 to 1999, an on-line setup was turned over to the production group where it only lasted six months. Since then, the low sodium in the control center, where each flame photometer is located, has been determined manually. Thus, this shows that the current method is not suitable for continuous, unattended monitoring. Moreover, the frequency of servicing and repair of the flame photometer is also very costly.

The ion-selective electrode method is a simple analytical technique for directly analyzing small concentrations of cation species, such as sodium (Na^+), in a solution. The ROSS Sodium electrode was used as the indicator electrode in conjunction with an 808 Titrando meter of Metrohm, which had an ISE-readout capability. Low level concentration standards from 0.02 ppm to 5.0 ppm Sodium were used for direct calibration of the instrument and consequently direct measurement of the sample concentrations. An ionic strength adjustor (ISA) was added in the form of NH_4Cl/NH_4OH solution. In this study, the ISE analysis of low sodium from steam condensate samples were compared to the atomic absorption (AA) results of the same samples. The method of preparing the standards and samples, including the addition of ISA, were documented in detail. Moreover, the care and maintenance of the ion-selective electrode was important during the course of the low sodium determinations.

1. INTRODUCTION

In analytical chemistry, substances are analyzed and the concentration or amount is determined quantitatively. One of the most popular measuring technique is potentiometry, which describes the measurement of potentials or voltages of electrochemical cells. In potentiometric measurement, the end point indicator is usually an electrode with or without a reference electrode. The membrane indicator electrode depends on a potential developed from an unequal charge buildup at the opposing surfaces of a special membrane. The charge at each surface is governed by the position of an equilibrium involving analyte ions, which in turn, depends on the concentration of those ions in solution. The immense value of this type of electrode depends on the ability to design and manufacture membranes that exhibit considerable selectivity toward a specific ion that produce potentials described by the Nernst-type equation. The excellent selectivity of these electrodes has led chemists to call these electrodes as ion-selective electrodes. The ion concentrations are obtained directly from the potential coming from this electrode. Such electrodes are relatively free from interference and provide a rapid and convenient means for quantitative estimations of important anions and cations.

The instrument most frequently used for sodium measurement is the sodium ion analyzer. A selective ion electrode similar to a pH electrode is used to measure the sodium content of the steam sample. In a typical operation, a regulated amount of an agent, such as ammonium hydroxide or DIPA, is added to a regulated amount of condensed steam sample to raise the pH and eliminate the possibility of hydrogen ion interference. A reservoir stores the conditioned sample and feeds it at a constant flow rate to the tip of the sodium ion electrode and then to a reference electrode. The measured electrode signal is compared to the reference electrode potential and translated into sodium ion concentration, which is displayed on a meter and supplied to a recording device. Electrode measurements are simpler and faster than other analytical techniques. The acceptance of the sodium ion analyzer as an accurate and reliable steam purity evaluation instrument is evidenced by its widespread use for continuous monitoring as well as for field testing. Many steam generating plants have switched from previously accepted methods to sodium ion analysis in order to improve accuracy. In comparison to other methods, such as atomic absorption (AA) or ion chromatography, the initial cost of setup is less and does not require additional expensive readout equipment. Moreover, these methods are equally adaptable to both laboratory and field use. In addition, sample color or turbidity does not affect the instrument.

The main goal of this study is to analyze the sodium content of steam condensate samples coming from the power plant using the ion selective electrode (ISE) method, and to eliminate doubts about H_2S interferences in the readings as shown by the closeness of the data with the AA determinations of the same samples. Consequently, this study can promote the use of an on-line sodium analyzer which utilizes the same ISE principle but uses a more sensitive ionic strength adjustor (ISA). The ISA used is in the form of di-isopropylamine (DIPA) which raises the pH of the solution to 11 pH units without contaminating the sample with sodium.

2. EXPERIMENTAL

To determine various detection limits required in method verification studies, seven replicates of 0.02 ppm Na were analyzed and the instrument and method detection limits (IDL and MDL), and limit of quantification (LOQ) were calculated. ID, which is the smallest signal that the instrument can distinguish from background noise, was calculated at 0.013 ppm. On the other hand, MDL, which is the minimum concentration that can be measured with a 99 percent confidence that the analyte is greater than zero, was determined at 0.013 ppm. In addition, the LOQ above which quantitative results may be obtained with a specified degree of confidence was established at 0.04 ppm. All detection limits were within the Power Plant limits for sodium below 1.0 ppm. However, values below MDL should be reported as below detection limit (<DL).

Replicates	0.02 ppm Na
1	0.028
2	0.023
3	0.020
4	0.028
5	0.024
6	0.021
7	0.017
Average	0.023
Std. deviation	0.004
IDL (s x 3)	0.013
MDL (t×sd); t(n-1, 1-α=0.99); t = 3.14267	0.013
LOQ (s x 10)	0.04

Table 1.0 IDL and MDL

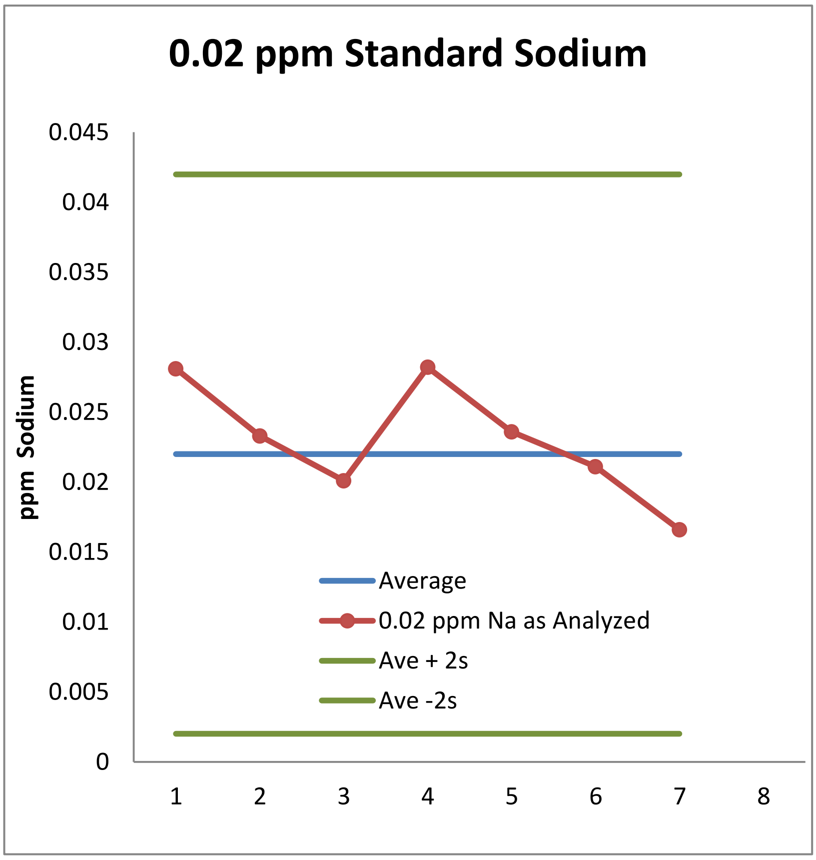

Figure 1: The figure above shows the 0.02 ppm sodium standard analyzed using the ISE method.

The sodium concentration in basic solutions can be measured under normal laboratory conditions down to 5×10^{-6} M (0.115 ppm). Measurements below 10^{-6} M must be made with extreme care as significant pickup of sodium may occur due to desorption from container walls as well as from dust and other contamination. Ordinary glass will dissolve sufficiently to produce spurious results at low levels. Plastic laboratory ware is recommended.

Table 2: Percent recoveries of spiked sample (sample concentration = 2.24 ppm, Spiking standard = 2.00 ppm)

2013-05-21	Spiked sample (ppm)	% Recovery
Replicate 1	2.23	111%
Replicate 2	2.13	101%
Replicate 3	2.13	101%
Replicate 4	2.14	102%
Replicate 5	2.14	102%
Average	2.15	103%

Percent recovery of spiked samples is an important tool for validating and assessing an analytical technique for particular sample types. A known amount of analyte (NIST traceable standard) is added (spiked) into the natural test sample matrix (brine sample) and its response is measured (recovered). The percent recoveries of five replicate samples, as shown by the equation below, range from 101 percent to 111 percent or an average of 103 percent, which is within acceptable limits.

$$\text{Percent Recovery} = \frac{(\text{spiked sample concentration} \times 2) - (\text{sample concentration})}{\text{Spiking standard concentration}} \times 100$$

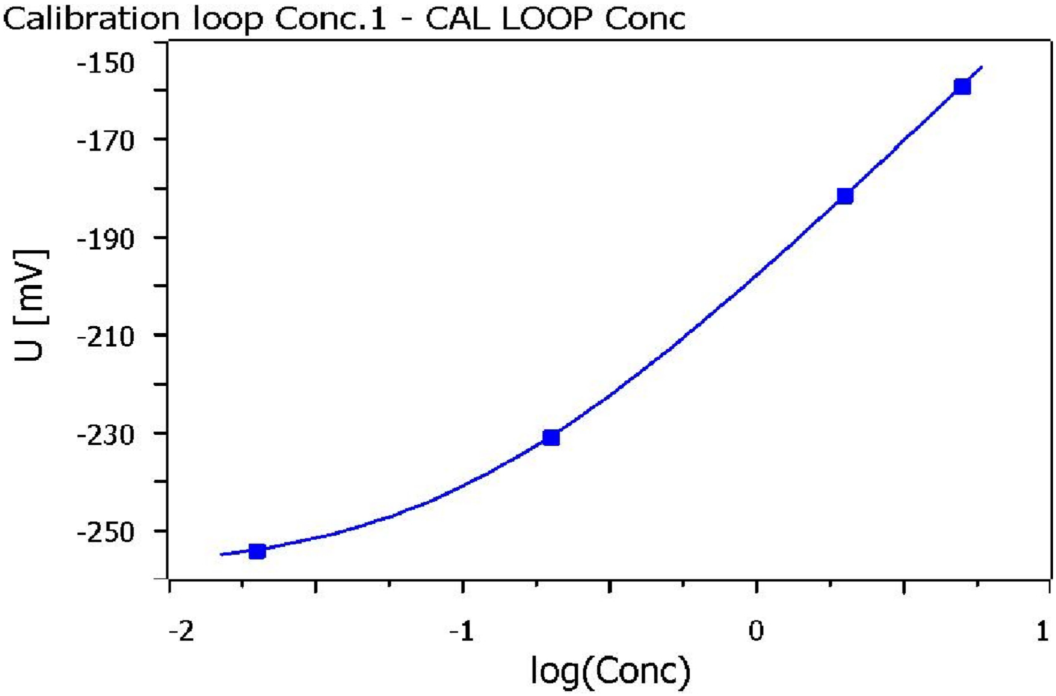

Figure 2: Low level sodium calibration curve using the Ion-selective electrode method.

Sodium concentrations in steam samples analyzed with ISE and AA on different dates were compared (Tables 3 and 4). In Table 3, the percent difference ranged from 0 to -25.0 percent. The sodium concentration with a -25.0 percent difference was already below the established MDL at 0.13 ppm. In addition, the percent difference in Table 4 ranged from 0 to 11.8 percent. For Table 4, the sodium concentration with an 11.8 percent difference was also below the established MDL. Except for these extremely low values, the percent difference of results between ISE and AA were within 10 percent, which was considered acceptable.

Table 3: Comparison of sodium results by ISE and AA (analyzed on day 1)

2013-05-10	ISE, ppm Na	AA, ppm Na	% Difference
Sample 1	0.32	0.29	-9.84%
Sample 2	0.10	0.10	0.00%
Sample 3	1.01	1.07	5.77%
Sample 4	0.68	0.65	-4.51%
Sample 5	0.09	0.07	-25.0%

Table 4: Comparison of sodium results by ISE and AA (analyzed on day 2)

2013-05-17	ISE, ppm Na	AA, ppm Na	% Difference
Sample 6	0.15	0.14	-6.90%
Sample 7	0.15	0.15	0.00%
Sample 8	1.53	1.48	-3.32%
Sample 9	0.17	0.16	-6.06%
Sample 10	0.87	0.86	-1.16%

Sample 11	0.16	0.16	0.00%
Sample 12	0.16	0.16	0.00%
Sample 13	0.08	0.09	11.8%
Sample 14	0.43	0.43	0.00%
	0.18	0.17	-5.71%

3. DATA ANALYSIS

Using data from Tables 3 and 4 and the data analysis statistical tool in Microsoft Excel, the F-test was used to test the null hypothesis that the variances of two populations were equal. The two populations were data from the ISE and AA analyses. The F-test is a test designed to indicate whether there is a significant difference between two methods based on their standard deviations. ***F*** is defined in terms of the variances of the two methods, where the variance is the square of the standard deviation.

$H_0: \sigma_1^2 = \sigma_2^2$
$H_1: \sigma_1^2 \neq \sigma_2^{2*9}$

F-Test Two-Sample for Variances

	ISE	AA
Mean	0.405333	0.398667
Variance	0.184655	0.18237
Observations	15	15
df	14	14
F	1.012533	
P(F<=f) one-tail	0.490869	
F Critical one-tail	1.583963	

If F >F critical one-tail, the null hypothesis is rejected. Based on the statistical evaluation, 1.012533 < 1.583963 (or F<F critical one-tail). Therefore, the null hypothesis that the variances of the two populations are equal is accepted.

If p<0.05, the null hypothesis is rejected. However, the p-value of 0.490869002 (p>0.05) shows that the measurements of sodium using ISE and AA methods are not significantly different or there is no difference between ISE and AA results. Figure 3 shows a comparison of ISE and AA results in graphical form.

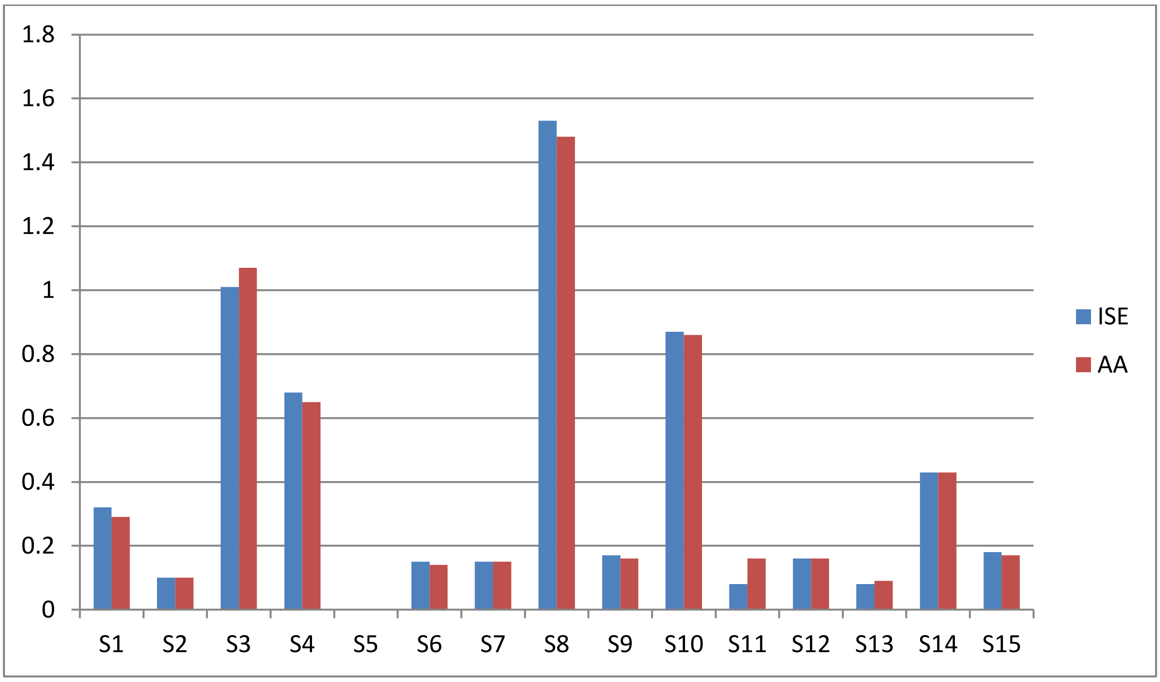

Figure 3: Comparison of ISE and AA results of samples 1-15 from Tables 2 and 3.

3.1 INSTRUMENTATION

The 808 Titrando (Metrohm) serves as the ISE meter attached to a PC Chemstation containing the Ti-Amo software. The ROSS Sure-Flow Sodium combination ion-selective electrode (Orion 8611BNWP), the low level Sodium electrode filling solution (90-00-12), the exchange unit dosing the 4M NH_4Cl/ 4M NH_4OH Ionic Strength Adjustor (ISA 475 mL 841111), and the magnetic stirrer compose the basic instrumentation needed to analyze the low sodium in steam condensate samples. The sodium rinsing solution used for rinsing the electrode is used since distilled water is not allowed for rinsing the glass sodium electrode. The commercial glass electrode responds strongly only to +1 cations. They are ineffective for +2 ions.

3.2 STANDARD PREPARATION AND CALIBRATION

3.2.1. Prepare a 100 ppm Na standard by diluting 10 ml of 1000 ppm Na standard (Orion 841108) to one liter.

3.2.2. From 10 ppm intermediate Na standard, prepare the following working standards. Measure 200 mL distilled water and add the following standards to prepare the working standards for calibrating the ISE electrode.

Table 4: The working standards for calibrating the Na ISE (added to 200 mL distilled water).

Step	Volume 10 ppm Na^+ standard added	Volume of 100 ppm Na^+ standard added	Concentration, ppm
1	0.4 mL		0.02
2		0.4 mL	0.20
3		4.0 mL	2.00
4		10.0 mL	5.00

3.2.3. From the above solutions, pipet 50 ml aliquot using the Handystep electronic pipet. Add 0.50 mL of ISA to each working standards. Measure the lowest concentration solution before the higher concentration solutions during calibration. The slope must be within 54-60 mV. For the samples, pipet 50 ml aliquot and add 0.50 mL of ISA. All standards and samples must be covered with parafilm. Use a plastic beaker as sample and standard containers.

3.2.4. The ISA can be prepared from the laboratory stock. Fill a 1000 mL volumetric flask up to the halfway mark with distilled water and add 214 grams of reagent-grade ammonium chloride (NH_4Cl). Under a hood, add 270 mL of concentrated ammonium hydroxide (NH_4OH), swirl the flask gently to dissolve the solid, and allow to cool. Fill the flask to the mark with distilled water, cap and upend several times to mix the solution.

3.3 STORAGE

For the routine storage of 8611BNWP ROSS Sodium electrode (1 week or less), soak the electrode in sodium electrode storage solution (Orion 841101) with 1 part to 100 parts deionized distilled water. Immerse both the tip of the electrode and the reference junction. Replace storage electrode filling solution (90-00-12) at a level which covers the coil. After storage, refresh the junction by pressing on the cap and letting a small amount of filling solution drain out. Replenish lost filling solution.

3.4 HAZARDS

pH adjusting reagents are strongly alkaline and volatile. Use normal eye and skin protection when handling ammonia, ammonium hydroxide, dimethylamine, di-isopropylamine (DIPA, this is sealed), monoethylamine, or morpholine.

3.5 SAMPLING

Regulate the temperature of samples that must be condensed, or cooled, or both, to a level between 15 ^oC and 40 ^oC. For highest accuracy, bring the sample temperature close to the temperature of the standards during calibration.

4. CONCLUSIONS

From the data obtained using the two methods, it is statistically proven that there is no significant difference between ISE and AA methods for analyzing low sodium in steam condensates. Since the electrode method is much simpler, safe, and easily hooked on-line, the authors are recommending ISE method for low Na analysis. The on-line sodium analyzer which uses the same principle is very suitable to be used in power plant monitoring of low sodium to replace the current practice of low sodium analysis by flame photometry.

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