

Sodium Monitoring in the Water and Steam Cycle of Power Plants

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ABSTRACT

Today sodium concentration has become one of the most important indexes for quality control of water and steam at power plants; however, measurement of this parameter can be difficult in practice. The use of ion selective electrodes means that analyzers are sensitive to pH shifts, and constant exposure to very low concentrations of sodium ions in ultrapure water conditions can lead to electrode desensitization. In addition, there is a need to address drift through regular calibration. This paper discusses the technical challenges in low level sodium analysis and the required features for a practical and accurate analyzer to provide trouble free, sub $\mu\text{g} \cdot \text{kg}^{-1}$ (sub ppb) measurement.

INTRODUCTION

Water quality is critical to the efficiency and performance of a steam generation plant and to the longevity of its associated equipment. Historically, simple conductivity measurement has been used extensively to monitor the quality of water, but for many plant chemists this has become insufficient to ensure the protection of high cost capital equipment. Today sodium concentration has become one of the most important indexes for water quality throughout the steam and water cycle in power plants. However, measurement of this parameter can be difficult in practice. For example, improvements in ion exchange resins over the past decade have now resulted in post mixed bed sodium levels below $0.03 \mu\text{g} \cdot \text{kg}^{-1}$ (0.03 ppb) [1]. Therefore there is a need not simply to measure low levels of sodium but rather levels that continuously remain at sub $\mu\text{g} \cdot \text{kg}^{-1}$ levels.

Several laboratory methods are available for sodium analysis; these include electrode potentiometry, ion chromatography, atomic absorption (ICP-AA) [2], and mass spectroscopy. Although laboratory analysis forms a part of the normal quality control process, it can require high demands of manpower and, by its nature, can only provide

information for a specific point in time. Therefore, most power plants will also employ on-line continuous monitoring.

The most economical and best practiced on-line method used for high purity water analysis is the potentiometry method, which uses a sodium ion specific electrode (ISE). In practice, temperature and pH fluctuations, fall-off in response in very low sodium concentrations, and difficulties maintaining calibration are all potential issues that must be addressed with an on-line analyzer. In fact, several techniques can be used to maximize the accuracy and efficiency of ISE analysis at a level as low as $20 \text{ ng} \cdot \text{kg}^{-1}$ (ppt, parts per trillion). This paper discusses the importance of sodium analysis and describes the key problems that need to be resolved in order to provide trouble free, sub $\mu\text{g} \cdot \text{kg}^{-1}$ measurement.

REASONS FOR SODIUM ANALYSIS

When sodium levels increase in high purity or ultrapure waters, it indicates the presence of unwanted dissolved impurities. In power plants these impurities can have catastrophic effects when deposits occur on turbine blades or on the heat exchange surfaces of the boiler.

In the all-volatile treatment (AVT) or oxygenated treatment (OT) boiler water cycle there are two direct ways in which sodium can enter the system: breakthrough from the water treatment process and condenser tube leaks.

Typical water treatment plants use ion exchange resins to remove unwanted inorganic compounds. Anion resins remove anion species such as chloride and sulfate; cation resins remove cations such as calcium and sodium. Sodium is the first cation that breaks through when the cation resin bed is exhausted. Measurement of the sodium level allows regeneration of the resin as required rather than by volume and/or time. This ensures that the water quality is always maintained, minimizes regenerant chemical (hydrochloric or sulfuric acid) costs and can prevent sodium-induced corrosion. Sodium analysis can also be used to detect accidental caustic release into the feedwater after anion column regeneration with sodium hydroxide [3]. Where water treatment plants incorporate reverse osmosis systems, sodium measurement can indicate possible membrane damage.

Sodium can also enter the boiler cycle through condenser tube leaks as most cooling waters contain sodium. Measuring sodium in the condensate pump discharge can allow early detection of feedwater or condensate excursions. Where condensers are followed with condensate

polishers, usually mixed beds, sodium can again be used to detect resin exhaustion and dissolved solids breakthrough.

In cycles with drum-type (circulation) boilers, phosphate treatment may be used. In this case sodium will be deliberately added in the form of sodium tri-phosphate. Sodium measurement in samples taken from the steam line at the boiler can be used to indicate carryover of dissolved impurities into the steam line.

It is evident that all of the excursions described above can have detrimental consequences for the power plant, and therefore some form of monitoring is required. Cation and specific conductivity are used frequently to detect all of the above excursions, but sodium analysis is much more sensitive. In the best cases, using conductivity measurement $0.02 \mu\text{S} \cdot \text{cm}^{-1}$ variations can be detected directly. This corresponds to $11 \mu\text{g} \cdot \text{kg}^{-1}$ sodium. A state-of-the-art sodium analyzer can measure below $0.1 \mu\text{g} \cdot \text{kg}^{-1}$ accurately; this is 100 times more sensitive than a conductivity measurement. If water quality is truly critical, then early warnings of excursions are also critical and sodium measurement should be the preferred option to minimize risk.

SODIUM ELECTRODE PRINCIPLE

Like all other ISEs, the sodium electrode relies on the change in potential arising from a change in ion concentration. This potential change is monitored versus a reference electrode (calomel or silver chloride reference). The sodium electrode is a glass electrode similar to a pH electrode with a special glass bulb sensitive to H^+ ions and also, to a lesser extent, to Na^+ ions. This glass bulb has a proprietary composition but contains Na^+ ions. The bulb is filled with a buffered solution at a fixed level of sodium ions. The difference in sodium concentration on both sides of the glass bulb membrane will be reflected by a change in potential. This potential change will be logarithmic with the concentration change (Nernstian response):

$$\Delta E = \frac{2.3RT}{nF} \log \Delta c \quad (1)$$

where E is the potential of the electrode, R the universal gas constant, T the absolute temperature, n the charge number of the electrode reaction, F the Faraday constant, and c the concentration of the sodium ion.

From this principle, it can be concluded that the pH will play a major role in sodium measurement. This point will be addressed in the section Proton Interference.

It is also clear that this type of sensor has no "physical zero." Since every sensor can be slightly different in terms of glass formulation (and change in time) or buffer composition, easy calibration will be required for accurate measurement.

All glass electrodes are also known to lose their sensitivity when they do not "see" the ion to be measured. This is particularly important where sodium electrodes are used for measuring very low sodium concentration in ultrapure

water applications. Different techniques can be used to revive the sensing electrode and are detailed in the section describing electrode desensitization.

PRINCIPLE OF OPERATION

Using sodium analysis in the industrial environment requires not only practical means of addressing the issues of pH, temperature and ISE responses but also the provision of a means of sampling, calibrating, controlling flow and controlling pressure in addition to making the instrument simple to use and easy to maintain for on-site personnel.

From the principles of operation described below it will be seen that the practical application of sodium ISEs has been directly addressed. In later sections of this paper more detail on the approach to some of the technical issues encountered will be discussed. *Figure 1* shows the schematic and basic functions of an on-line sodium analyzer.

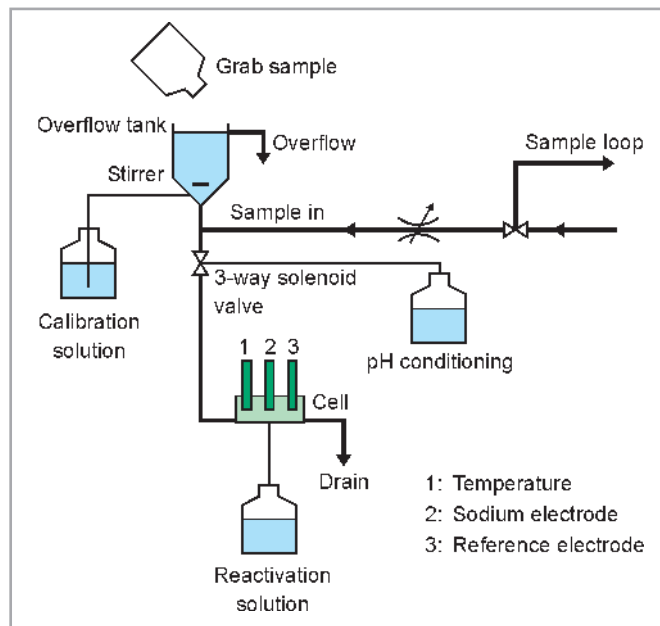


Figure 1: Schematic and basic functions of an on-line sodium analyzer.

Measurement Mode

In normal measurement mode the sample is injected at the bottom end of the overflow tank with excess sample flowing into the overflow tank and then to the drain. A measured fraction of the sample is mixed with the pH conditioning reagent as it flows down to the measuring cell. This ensures that the sample is always measured under optimum pH conditions. The first well of the measuring cell contains a thermistor that measures temperature. The second well contains the sodium ISE, and the third well holds the reference electrode. At the exit of the measurement cell, the sample is collected and sent to drain. After temperature compensation the sodium concentration is calcu-

lated from the differences between the sodium ISE and the reference electrode.

Reactivation Mode

As the analyzer is designed for use in ultrapure water applications it is expected that the sodium ISE will normally be measuring very low concentrations of sodium over long periods of time. It has been indicated that this can lead to the sodium ISE becoming "sleepy" and unable to respond to changes in sodium concentration. To avoid this, an automatic reactivation can be programmed. A concentrated reactivation solution is injected into the sodium ISE well of the measuring cell. After 5 minutes a sample flow will resume and rinse off the reactivation solution and the instrument will return to normal measurement mode.

Automatic Calibration Mode

All analyzers require periodic calibration. To minimize operator involvement, automatic calibration can be programmed. The first step of the calibration process is reactivation (see previous paragraph). Following rinsing, and once a low level sodium value with a signal stability is achieved, the process water running through the overflow tank is trapped. A known level of sodium is then injected into the overflow tank and then the thoroughly mixed solution passes to the measuring cell. A second calibration solution is prepared in a similar way but with an injection of a concentration of sodium ten times higher. With the result of this second calibration sample the instrument will compute the new calibration coefficients and switch back to measurement mode.

Manual Calibration Mode

Although automatic calibration can be programmed it may also be necessary from time to time to carry out a manual calibration. The calibration process is initiated by the operator and the prompts on the control screen indicate when each of the two calibration solutions should be added into the overflow tank. It is necessary for the operator to also enter the value for the concentration. The two calibration solutions should be of different concentrations, normally the second having a sodium concentration ten times greater than the first solution. As with the automatic calibration the instrument will compute the new calibration coefficients and switch back to measurement mode.

Grab Sample Mode

The manual calibration facility also allows the instrument to be used for one-off measurements in a grab sample mode. Manual initiation of this

mode of operation interrupts the sample flow and the overflow tank is drained. The operator is prompted to pour the sample into the overflow tank. The normal measurement cycle proceeds. The instrument automatically returns to continuous measurement mode once the result has been obtained.

PROTON INTERFERENCE

A sodium ion selective electrode is essentially a pH electrode with sensitivity to alkaline ions. For this reason, sodium ion selective electrodes are also highly sensitive to protons. The lowest detection limit is consequently dependent on the pH of the sample. Typical electrodes have a selectivity coefficient at or below 150, meaning that they are 150 times more sensitive to protons (hydrogen ions, H^+) than to sodium ions, Na^+ . At a pH of 11.0, an electrode with a selectivity coefficient of 150 will give an offset of $0.035 \mu g \cdot kg^{-1}$ on the sodium reading. For this reason it is very important to keep the pH as high as possible when measuring sub $\mu g \cdot kg^{-1} Na^+$ concentrations.

To ensure accurate, repeatable sodium measurements, pH must be constant and preferably maintained at or above pH 11.0. For obvious reasons, sodium hydroxide cannot be used. The most effective way to condition the sample water is by injecting vapor of diisopropylamine (DIPA) to obtain a high pH level without sodium contamination.

It is important to understand that, as a gas, the solubility of DIPA in a measured sample depends on the temperature. From a given volume of gas and a given volume of liquid mixed together, if liquid temperature decreases the dissolved gas quantity increases (from Henry's law). In reverse effect, when the temperature increases the pH level has a tendency to decrease and the lowest detectable concentration of sodium will be higher. To maintain a low detection limit it is important to add more DIPA when the sample temperature increases.

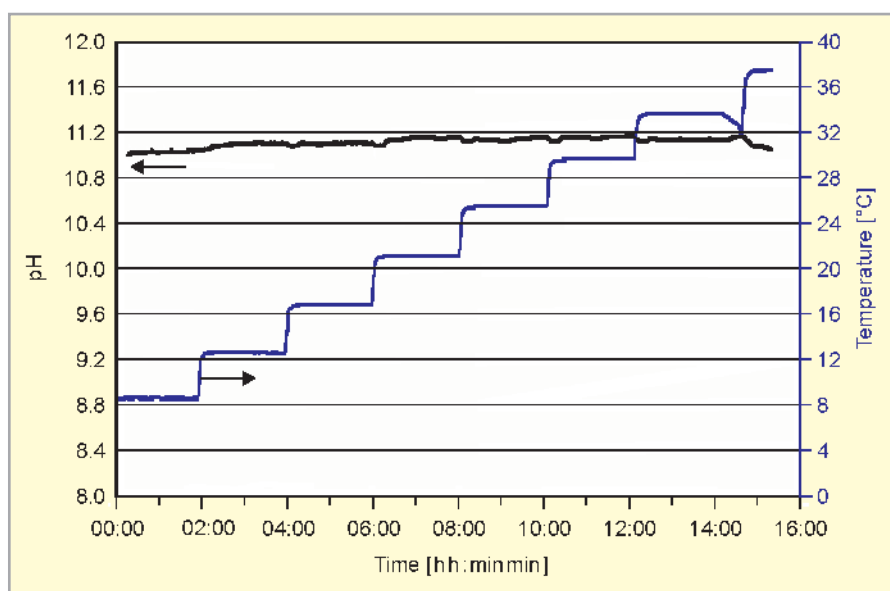


Figure 2: Temperature compensated pH using a 3-way valve control.

Using the siphon effect of the liquid sample column, DIPA is mixed with the sample without using any pump or pressurized gas. Then a fine tuning of the siphon effect is performed using a 3-way valve. This 3-way valve system has the advantage of modifying the gas/liquid ratio whilst simultaneously maintaining a constant level of pH even at higher values and with a sample temperature found in power plants or semi-conductor applications. *Figure 2* shows the pH of a sample after conditioning during temperature ramping and confirms the efficacy of this approach over a 30 °C temperature range.

DIPA addition can be automatically controlled to compensate temperature swings or for application at high sodium levels. The sodium ISE will always be in a stable pH environment thus increasing stability in sodium readings. The introduction of the 3-way valve responds to the need for the lowest detection limit independent of temperature swings and offers optimal and stable pH conditioning whilst minimizing DIPA consumption for a given application, thus ensuring a more repeatable and accurate analyzer.

REDUCING ELECTRODE DESENSITIZATION

In the well-controlled steam and water cycle it is normal for a sodium analyzer to be exposed to very low levels of sodium over long periods of time. This can lead to desensitization of the electrode and hence a reduced response to changes in sodium concentration. This effect is sometimes referred to as that of a "sleepy" electrode.

A sodium ISE is a glass electrode and on the surface of the bulb at the end of the electrode is a hydrosilicate gel layer containing sodium. When such electrodes are exposed for a long time to liquid containing sodium concentrations lower than $0.5 \mu\text{g} \cdot \text{kg}^{-1}$ – $1 \mu\text{g} \cdot \text{kg}^{-1}$, the sodium within the gel structure gradually leaches out. The ability to reflect changes in sodium in the sample decreases strongly when the sodium concentration in the gel layer decreases. An early consequence of this change in the gel layer is the lengthening of response time. It may take several hours to respond to a $10 \mu\text{g} \cdot \text{kg}^{-1}$ step change [4].

Figure 3 shows a new sodium ISE exposed to a flow of pure water at room temperature. A steady injection of $100 \mu\text{g} \cdot \text{kg}^{-1}$ sodium is made. On Day 0, the response time is within 2 minutes and the concentration is followed to observe the response time evolution 3 days later and 5 days later. The curves show the response time doubled after only 3 days and doubled again after 5 days.

A classic reactivation technique is etching: using chemically corrosive solutions to remove outer layers of the gel and reach a layer that still has sodium in it. This causes embrittlement and premature loss of probe life. These etching solutions contain fluoride, which is dangerous and must be handled with care in a correct environment [4].

An alternative method is to expose the electrode periodically to a solution containing substances appropriate for regeneration of the gel layer, which in turn avoids any chemical polishing solutions. The result of this treatment is shown in *Figure 4*.

It can be seen that response time to an injected solution of $100 \mu\text{g} \cdot \text{kg}^{-1}$ is maintained throughout the period of the test when reactivation of the gel layer is undertaken. Maintaining the gel layer at any time will eliminate sluggish responses during calibration, eliminate the need for hazardous solutions and ensure a rapid response by the analyzer.

CALIBRATION

Two-Point vs. Single-Point Calibration

All sodium analyzers currently on the market require periodic calibration because all ISEs have a tendency to drift over time. A two-point calibration with a tenfold difference in concentration is usually performed due to the Nernstian (logarithmic) response of the glass electrode. Once the electrode potentials at the two concentrations have been measured, temperature correction is made and an iterative calculation can be applied to account for the background sodium concentration in the "pure" water. This type of calibration yields a slope (xx mV per decade) and an offset

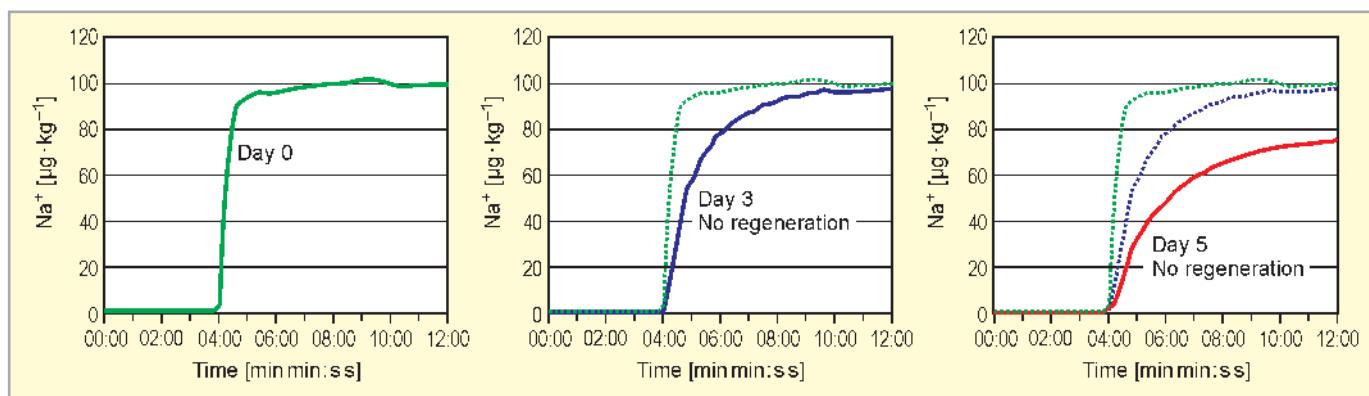


Figure 3: Loss of sensitivity and degradation of the response time of a sodium electrode in a very low sodium environment ($< 0.03 \mu\text{g} \cdot \text{kg}^{-1}$).

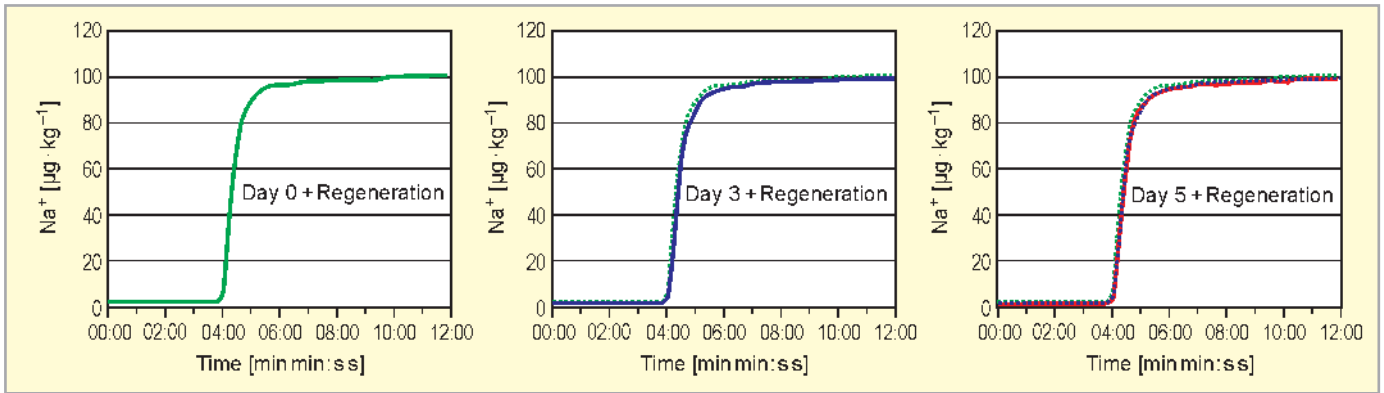


Figure 4: Effects of the proprietary reactivation method under identical conditions to Figure 3.

value (yy mV at $1 \mu\text{g} \cdot \text{kg}^{-1}$). The use of an automatic two-point calibration can ensure satisfactory operation without the need for operator action. However, if only one parameter seems to change with time, it could be simpler to calibrate with a single-point calibration. Both options can be made available to the operator.

Standard Concentration Range for Calibration

Calibrations are usually performed at a concentration close to the useful measuring range. For the targeted applications, measurements are generally in the $\mu\text{g} \cdot \text{kg}^{-1}$ to sub $\mu\text{g} \cdot \text{kg}^{-1}$ range. However, preparing standard samples in this range is difficult and risky: water used for the dilution is never sodium free and the packaging and handling of the samples is another source of sodium contamination. In practice it has been found that a set of $100 \mu\text{g} \cdot \text{kg}^{-1}$ –

$1\,000 \mu\text{g} \cdot \text{kg}^{-1}$ calibration points is the optimal trade-off in order to obtain the best accuracy, even in the lowest measuring range. Figure 5 below shows a series of calibration cycles performed over a 10-day period. During the first 4 minutes, process water sample is flowing through the instrument. After 4 minutes, a $100 \mu\text{g} \cdot \text{kg}^{-1}$ solution, previously poured into the overflow vessel, is running on the electrodes. At time $t = 12 \text{ min}$, another $1\,000 \mu\text{g} \cdot \text{kg}^{-1}$ sodium solution is injected into the system. The 3 voltages recorded during this process are used to compute the calibration parameters.

Flow Injection vs. Volumetric Calibration Sample Preparation

Most sodium analyzers require a flowing sample for accurate and fast analysis. A simple calibration method would

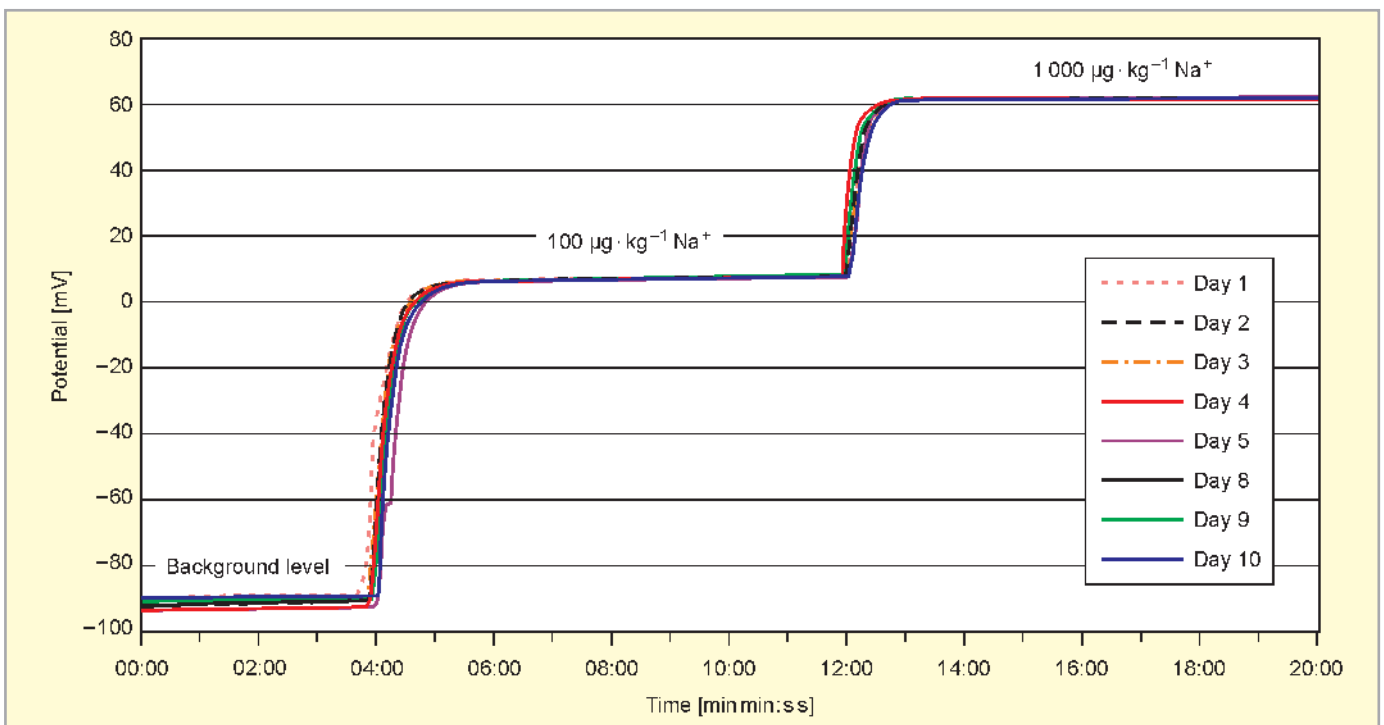


Figure 5: Series of calibration cycles performed over a 10-day period

be to inject a fixed flow of known sodium ion solution into a measurement stream. However, this method directly relies on the accuracy of the flow meters, which are rather costly and sensitive. Where an overflow vessel is available it is much more feasible and accurate to inject a known volume of sodium ion solution into a precisely known volume of vessel. Various sodium concentrations can be reliably prepared and sequentially measured, depending on the volume of the sodium solution injected into the overflow tank. $100 \mu\text{g} \cdot \text{kg}^{-1}$ and $1\,000 \mu\text{g} \cdot \text{kg}^{-1}$ sodium solutions have been found to give effective results for automatic calibrations of this kind.

Automatic vs. Manual Calibration

Once a sodium analyzer is fitted with the necessary features (overflow tank, control valves, injectors for sodium solution), the calibration process can easily be automated. It can be programmed in such a way that the blind period during the calibration does not disturb the normal operation of the process being monitored. The preferred master solution injected in the overflow tank contains $10 \text{ mg} \cdot \text{kg}^{-1}$ (ppm) sodium ions. This type of solution is easy to prepare and less sensitive to contamination from the environment and from the container. With only a low volume of master solution injected per calibration, the calibration bottle will last a long time. Some end users will prefer a manual check or a manual calibration for the use of their instrument, which can easily be conducted using the overflow tank and prepared or commercial standard solutions.

CONCLUSION

The critical issues of pH, temperature and desensitization of the sodium ISE electrodes can be overcome in a practical manner suitable for industrial, on-line applications.

Actively controlled DIPA addition with temperature compensation eliminates errors due to pH and temperature fluctuations. The use of frequent reactivation of the electrode eliminates the need for etching and reduces electrode desensitization, thus maintaining response time even when the electrode is subject to long periods of low sodium concentration.

In addition, the introduction of fully automatic calibration using an easy to prepare $10 \text{ mg} \cdot \text{kg}^{-1}$ standard has been shown to not only reduce calibration error but also to ensure long-term accuracy of measurements

The work described in this paper has provided the technical foundation for a new sodium analyzer that offers on-line industrial performance with the maximum accuracy and efficiency of ISE analysis at a level as low as $20 \text{ ng} \cdot \text{kg}^{-1}$ (ppt, parts per trillion).

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