

# On-Line "Reagentless" Amperometric Method for Determination of Bromine in Spas

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*The main challenges in developing a method for bromine control in the spa environment are that the method has to be non-invasive (method itself does not alter the composition of the "process" stream) and reliable. Unfortunately, the currently available oxidation-reduction potential (ORP) based systems, while non-invasive, are often not reliable since many factors limit the interpretation of the values obtained. The correlation between the ORP measurements and halogen concentrations is impaired due to the irreversibility of many electrochemical processes, electrode poisoning, the presence of multiple redox couples and due to the very small exchange currents that are logarithmically related to the analyte concentration.*

*Amperometric measurements have significant advantages over the ORP ones. Due to high selectivity, low detection levels, modest cost and often direct analyte quantitation, amperometry has become an exceptionally powerful laboratory tool. However, the extrapolation from the lab unit to the on-line process analyzer/controller is by no means straightforward mainly since one still has to address the problem of potential electrode poisoning.*

*This paper discusses the development of a novel robust "reagentless" amperometric method for bromine control in spas that relies on the use of a versatile inexpensive potentiostat which can be programmed to execute a complex potential waveform. This waveform includes an electrode regeneration/stabilization*

*step and an analytical/diagnostic step. To the best of our knowledge, the amperometric system described in this contribution is the first application for direct, reagentless on-line method for control of halogens using membraneless sensors.*

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## Introduction

Strict control of oxidizers/sanitizers is of paramount importance to assure bathers' health and safety. In order to be successful, a system for bromine control in spa environment has to meet the following criteria:

1. System should require no user calibration or adjustment (unattended operation).
2. System should operate reliably in hard water conditions without sensor cleaning.
3. System should control bromine at 3–5 ppm levels.
4. Sensor life should be two years without maintenance or access to the spa equipment.
5. System has to be low cost

Several analytical methods/technologies may potentially be utilized:

1. Spectrophotometric/colorimetric
2. Amperometric titrations
3. ORP
4. Amperometric and/or voltametric

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## Spectrophotometric/Colorimetric Methods and Amperometric Titration Methods

Very good spectrophotometric/colorimetric analytical methods for determination of chlorine and bromine have been developed for laboratory and other off-line applications (Gordon *et al.* 1992, APHA 1995). However, it is difficult to modify these methods for on-line applications. These methods require the use of reagents that have to be replenished regularly. The reagents often cannot be discharged into the spa water due to their toxicity. This in turn requires separate "plumbing" for the analytical system. The enumerated problems make spectrophotometric/colorimetric-based systems prohibitively expensive for the on-line oxidizer/sanitizer control in the spa environment.

Excellent laboratory titration methods for determination of bromine and chlorine with amperometric end-point detection have been developed (Gordon *et al.* 1992, APHA 1995). Unfortunately, the modification of these methods for on-line application is not straightforward due to concerns similar to those discussed for the spectrophotometric/colorimetric analytical methods. The amperometric titration methods also use reagents that have to be replenished regularly. The reagents cannot be discharged into the spa water due to their toxicity. In addition, titration methods are inherently difficult to automate. The enumerated problems make titration-based systems with amperometric end-point determination prohibitively expensive for the on-line oxidizer/sanitizer control in the spa environment.

## Oxidation-Reduction Potential (ORP) Measurements

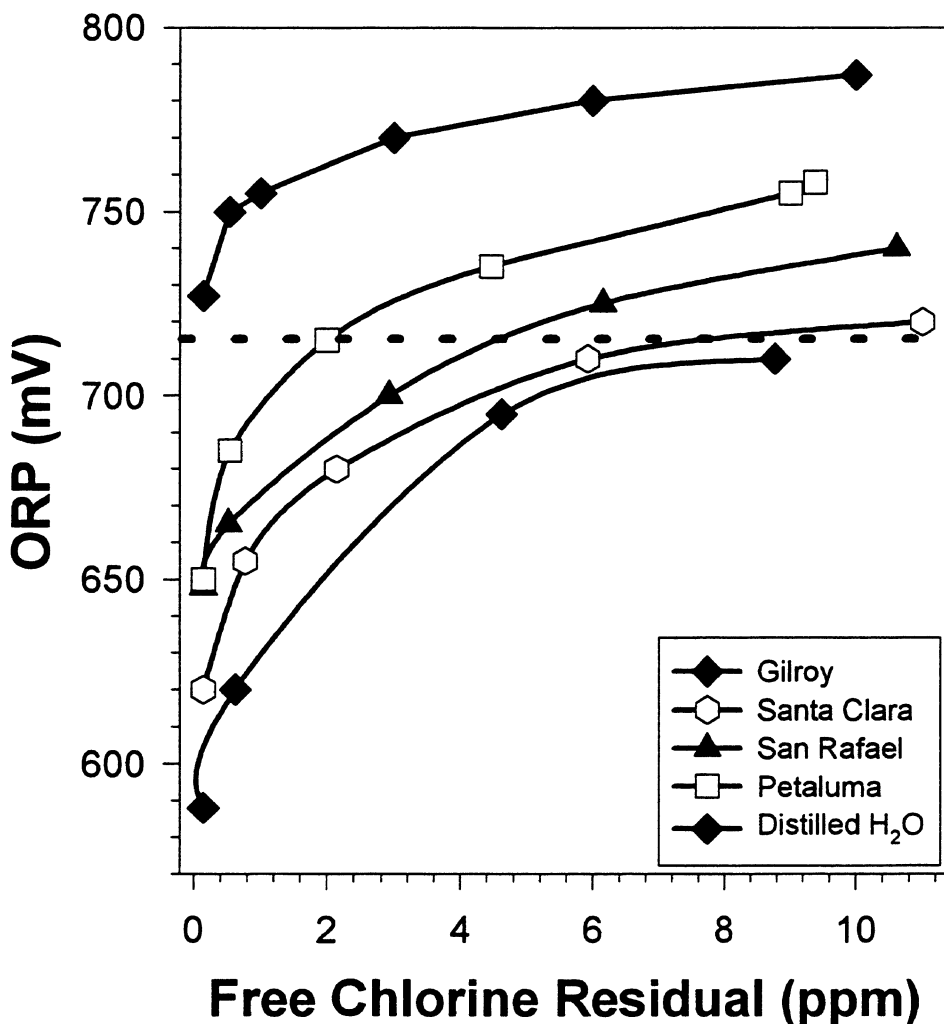


Figure 1 – ORP vs. chlorine concentration at pH 7.5 as a function of water type (adapted from White 1992)

Control of the oxidizing sanitizers using potentiometric ORP measurements is ubiquitous. A combination of a platinum-working electrode and usually a silver/silver chloride reference electrode is utilized for unattended ORP measurement. The ORP measurements are instrumentally straightforward. However, many factors limit the analytical interpretation of the ORP data. It is often impossible to correlate the actual bromine and chlorine concentrations to the oxidation-reduction potential measured for a given sample. Working-electrode poisoning is probably the most troublesome. Of course, for laboratory ORP determination simple polishing of the platinum surface can alleviate this condition. Unfortunately, in an on-line application polishing is not feasible if one strives for unattended operation. Other constraints in analytical interpretation of the ORP data are small exchange currents that are logarithmically related to the analyte concentration

and presence of multiple redox couples in the real world systems. Presence of inert redox couples and/or electrochemically irreversible processes further hinder the utility of the ORP measurements. In other words, the assumption of a reversible chemical equilibrium, fast electrode kinetics, and the lack of interfering reactions are essential for chemical interpretations of the oxidation–reduction potentials (APHA 1992). Unfortunately, these conditions rarely, if ever, are met in real world systems.

Figure 1 summarizes the calibrations performed using an ORP probe in four different municipal waters (White 1992). For comparison purposes calibration in distilled water was also performed. For the sake of argument, let us assume that a given ORP sensor is calibrated in Petaluma water at 2 ppm level. The same probe would read nearly 5 ppm chlorine in the spa that uses San Rafael water, and nearly 8 ppm in Santa Clara water. In the spa with Gilroy water the chlorine level would probably be higher than 10 ppm. If the ORP probes were calibrated in distilled water to which chlorine was added and if these probes were used for controlling electrolytic chlorine or bromine generation, it is clear that the production of sanitizer would be continuous. This, of course, could have unfortunate consequence of having dangerously high levels of halogens in the spa water.

Here is what Geo. Clifford White, the author of the Handbook of Chlorination and Alternative Disinfectants (White 1992), had to say about ORP measurements: "...There is only 37 mV difference in the ORP values between 1 and 4 mg/L chlorine residual. It is obvious that such a system will be inherently difficult to control. However, there is another factor to be considered. A free chlorine residual tends to "poison" the ORP cell. This reduces the sensitivity of the cell which retards the cell response to changes in chlorine residual and pH". Also: "...Since the above investigation illustrates that every water has a different ORP "poise", *each installation has to be calibrated to that poise*. If the water source or the character of the water is changed a new calibration must be made. This further demonstrates the fact that the *ORP control method is qualitative and not quantitative*." One might argue with the author whether the "free chlorine residual" poisons the platinum working electrode, or the actual culprits are some other species, but one has to agree with the conclusion that ORP measurements have serious constraints, especially when applied for the on–line control of halogens.

## Amperometric Method for Bromine Control in the Spa Water

Since none of the systems described above satisfied the criteria for reliable bromine control in spas, BioQuest decided to investigate the use of

amperometric–based systems.

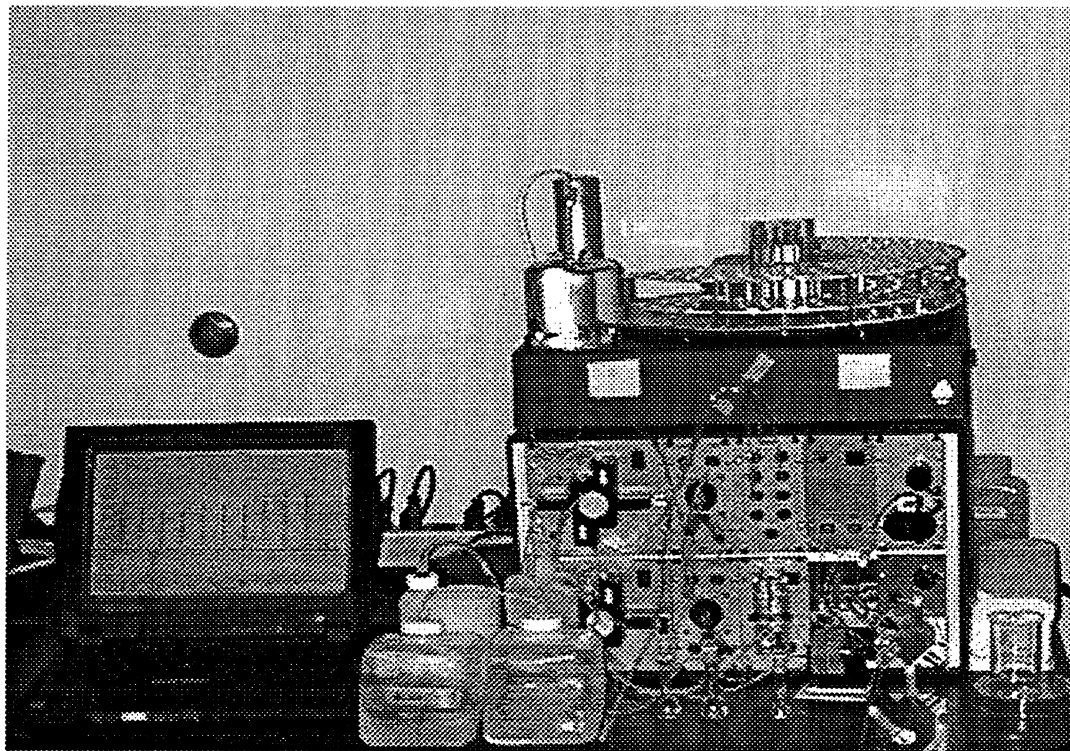
Here is what Dr. Kissinger, the founder of Bioanalytical Systems, Inc., a company that manufactures laboratory electrochemical systems, said in his recent monograph (Kissinger and Heineman 1996): "It is now clear that electrochemical measurements can often have significant advantages over the classical spectroscopic approaches. Amperometry can be more specific, therefore, lower detection limits are often feasible. Because electrochemical detectors do not require optical carriers, they can be less expensive than the UV/VIS absorption or fluorescence detectors. This is especially true when one considers that electrochemical detectors are inherently tunable without the need for such things as monochromators or filters. However, there is a lack of acceptance by chemists weaned on Beer's law. On the other hand, amperometric methods in biochemistry are just beginning to be commercialized, and it is now certain that they will come into widespread use".

An amperometric detector is one in which potential applied to the detecting (working) electrode is held constant and the resulting current is measured as a function of time. A voltametric detector is one in which the applied potential is varied with time and the current response is measured as a function of both time and applied potential. Our system actually employs both modes because the applied potential is varied. However, the actual bromine measurements are performed at the near–steady state at the time when the charging current due to the potential step has decayed significantly so that the faradic current component due to the bromine reduction is dominant.

The advantages of the amperometric sensors are:

1. Selectivity.
2. Low detection levels.
3. Modest cost.
4. Direct analyte quantitation.
5. Zero current corresponds to the absence of the analyte.

Selectivity relates to the inherent tunability of the amperometric detectors. The analyte has to be electro–active (reducible or oxidizable) at the potential applied at the working electrode. Amperometric laboratory units often can determine low ppb ( $\mu\text{g/L}$ ) levels of the analytes. Direct analyte quantitation relates to the potential of using "reagentless" methods, which are inherently applicable to the on–line or *in-situ* monitoring and control. In this respect, amperometry is similar to the NIR methods utilized extensively in the petroleum and organic synthesis industries. The additional advantage of the amperometric on–line methods that we are developing is that these methods are non–invasive in the



**Figure 2 – Amperometric cyanide analyzer (USEPA Method OIA-1677).**

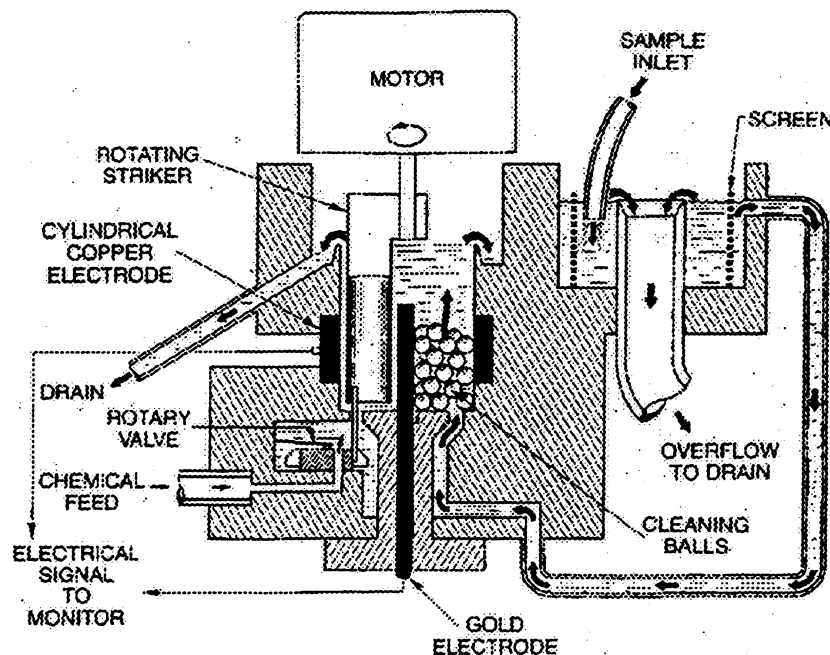
sense that they do not alter the composition of the “process” stream.

Amperometry is an exceptionally powerful analytical laboratory tool. The apparatus depicted in Figure 2 determines available cyanide using the USEPA Method OIA-1677 (Milosavljevic, *et al.* 1995, Federal Register 1999). The limit of detection for this amperometric-based system is less than 1 ppb with a throughput of over 45 analyses per hour. However, the extrapolation to the process analyzer/controller for in-situ analyses of bromine, which in a strict sense our system is, is not straightforward. First and foremost is the price. The unit depicted costs over \$40,000. How does one go about designing a system that should cost two orders of magnitude less? In addition, if the signal in the laboratory cyanide analyzer deteriorates, one stops the flow injection system, disassembles the amperometric flow-through cell and regenerates the electrode by polishing. In the on-line analyzer, of course, one does not have this

both the cost and the reagent disposal issue preclude the use of these systems for halogen controls in the spas.

luxury. The electrode regeneration is addressed in the unit designed to measure chlorine that is schematically shown in Figure 3.

This basic amperometric design has been utilized since the 1960's and has been updated throughout the years. It uses cleaning balls to clean and regenerate the electrode as necessary and it also has a rotating striker. This is not a reagentless *in-situ* system since buffer has to be added. Hence,



**Figure 3 – Chlorine amperometric analyzer (adapted from White 1992).**

Another way to deal with electrode deactivation (poisoning) issues is to use membrane type sensors similar to Clark's amperometric oxygen probe (Hitchman 1978). The membrane type sensors can be used for *in-situ* halogen analysis since membrane prevents electrode fouling that would result in the decrease of the amperometric signal. The problems of membrane probes are clogging of the membranes and maintenance requirements of replacing them. In addition, these probes have relatively slow response times since the analyte has to diffuse through the membrane to reach the working electrode of the amperometric sensor.

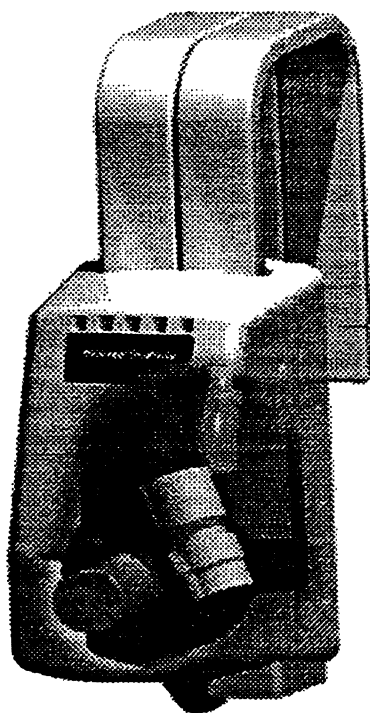
In our amperometric sensor design we rely on using electrochemical technique for regeneration and stabilization of the working electrode. It has been established almost two decades ago that it is possible to clean certain types of electrodes electrochemically (Hughes and Johnson 1981). However, in order to do this one needs very expensive equipment and these techniques have been utilized mainly for determining electroactive species separated by high-performance liquid chromatography including ion-chroma-

tography (LaCourse 1997). To the best of our knowledge, these techniques have not been successfully implemented for the unattended on-line analytical instrumentation.

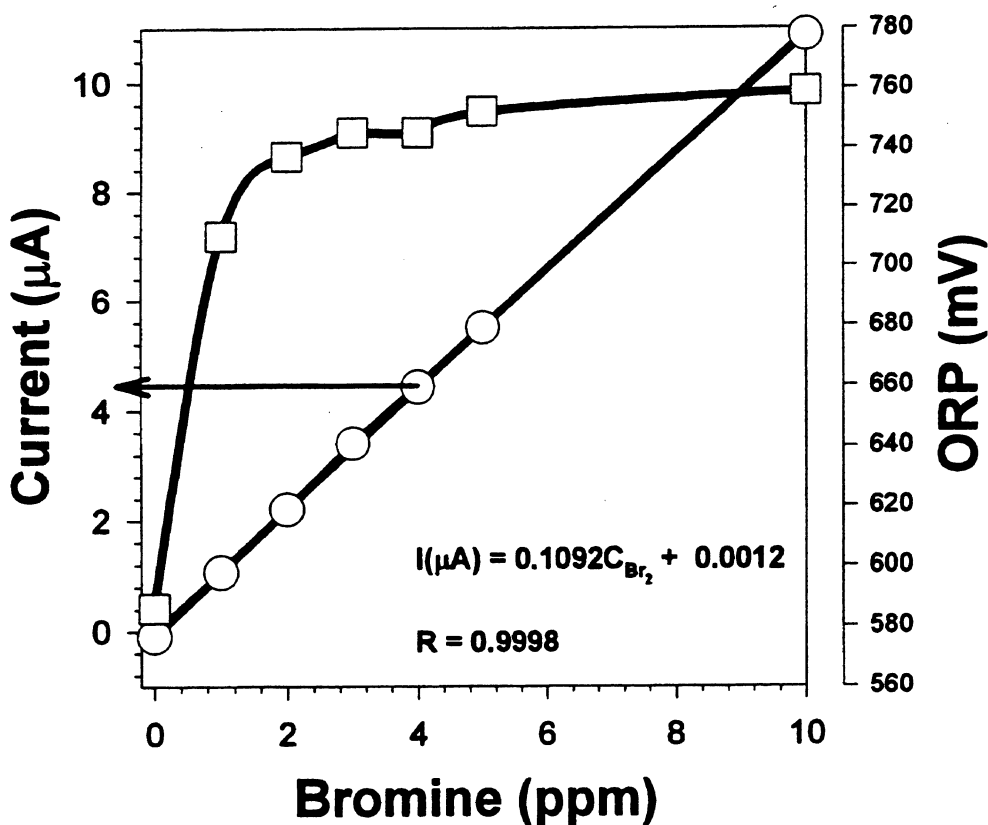
The successful design and production of a versatile inexpensive potentiostat that can be programmed to execute essentially any combination of wave-forms that the analyst desires was a cornerstone in developing reliable *in-situ* reagentless technique for bromine control in the spa water. In its latest embodiment our amperometric sensor system for bromine control has two potential waveforms. One of these is designed for electrode regeneration and stabilization and the other is an analytical staircase potential waveform. The currents measured at various potentials in the latter cycle are used for quantifying the bromine levels, as well as for the diagnostics of the sensor performance.

Figure 4 illustrates the retrofit modification of the complete bromine sanitation system. The system contains the electrolytic bromine generating system that includes a rotating anode that also acts as an independent solution pump. The external and internal plastic tubing conduits, besides re-circulating spa water through the electrolysis system, serve the purpose of continually flushing the amperometric probe with the spa water. The amperometric sensor is equipped with graphite working and counter or auxiliary electrode and the Ag/AgCl double junction reference electrode.

Figure 5 summarizes the calibration comparison in the 0–10 ppm bromine range using our amperometric system and an ORP probe. From the figure it may be seen that there is very small potential change in the 3–6 ppm bromine interval for the ORP measurements. This, of course, means that this system can not reliably determine the changes in bromine levels in this range. In contrast, the amperometric system gives linear current/concentration dependency throughout the range tested. This means that it has the same high sensitivity ( $\sim 0.1$  mA/ppm) throughout the linear dynamic range of the method. Sensitivity is defined as a signal (current) change per concentration unit. Also, the correlation coefficient measuring the goodness-of-fit is better than three nines. The intercept of the line is, within the experimental error, equal to zero, which means that the zero current (signal) correspond to the absence of the analyte. Or in analytical terms, blank produces zero detector output. As was illustrated before this is not true for the ORP measurements (for details please see Figure 1). The linear dependence between bromine concentration and detector signal and zero signal for the absence of the analyte give us the luxury of the *ex-situ* calibration of our sensors. As was pointed out earlier by Geo. C. White, this is not the case for the ORP probes that have to undergo *in-situ* calibration and frequent calibration checks.



**Figure 4 – Retrofit bromine sanitation system that includes an amperometric sensor for continuous bromine control.**



**Figure 5 – Calibration comparison:  
Amperometry vs. ORP**

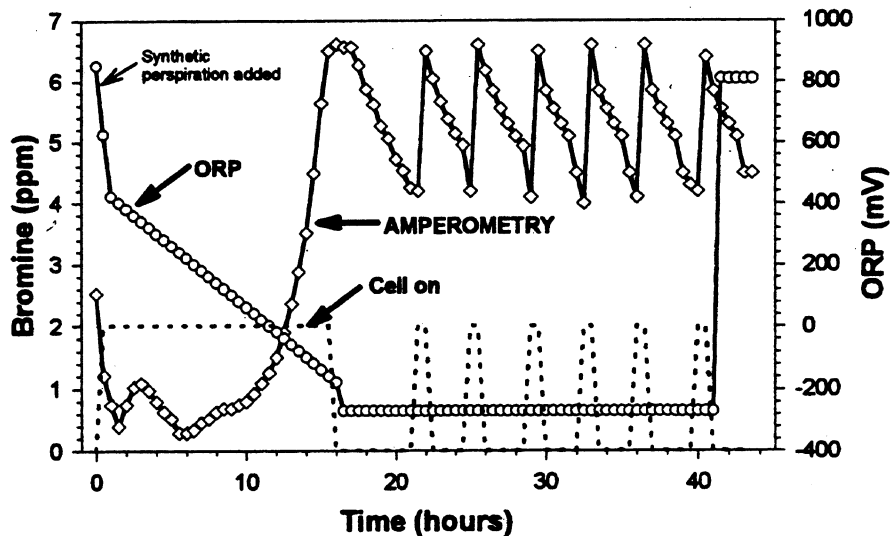
Figure 6 illustrates the ORP/amperometry comparison for the long-term spa test. The dashed line indicates when the electrolytic production of bromine is on (value 2) or off (value 0). The response of the amperometric sensor is depicted with diamond symbols, whereas the response of the ORP probe is depicted with circle symbols. Synthetic perspiration (prepared and dosed according to White 1972) was added almost at the beginning of the experiment. As expected, a decrease in bromine concentration occurs and the electrolysis cell is turned on producing bromine. The amperometric trace indicates the rise in bromine levels; the ORP probe does not. It is obvious that the latter probe has been deactivated (poisoned) by the components of synthetic perspiration. The ORP probe begins reading elevated levels of bromine only near the end of the 45-

hour experiment. As you can see the amperometric trace essentially follows on-off states of the electrolysis cell. It is not difficult to imagine what would have happened if the ORP was controlling the bromine generating electrolysis system – the over-bromination would have occurred. Fortunately, in this experiment the amperometric sensor controlled the electrolysis system.

**Conclusion**

We believe that the following were the milestones in successful development of the reliable method for bromine control in the spa environment:

1. Development of a versatile inexpensive potentiostat that can be programmed to execute essentially any



**Figure 6 – Comparison of the ORP and amperometry in the long-term spa test**

- combination of waveforms.
2. Development of an electrode regeneration/stabilization waveform.
  3. Development of an analytical diagnostic staircase waveform.
  4. Development of a simple amperometric sensor.

To the best of our knowledge, the amperometric system described in this contribution is the first application for direct reagentless, on-line (*in-situ*) method for halogen control using a membraneless amperometric probe. This statement can probably be extended to include any analyte. In addition, we are optimistic that the on-line amperometric methods that we are developing will find widespread use in such fields as spa, pool, and cooling tower control.

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