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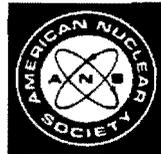
Fifth International Symposium on Environmental Degradation of Materials in Nuclear Power Systems – Water Reactors

NACE
National Association of Corrosion Engineers

TMS
Minerals • Metals • Materials

August 25-29, 1991
Doubletree Hotel • Monterey, California

LABORATORY VERIFICATION OF ON-LINE LITHIUM ANALYSIS USING ULTRAVIOLET ABSORPTION SPECTROMETRY

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ABSTRACT

Several laboratory experiments were performed to evaluate the capability of absorption spectrometry in the ultraviolet-visible wavelength range with the objective of developing methods for on-line analysis of lithium directly in the primary coolant of Pressurized Water Reactors using optical probes. Although initial laboratory tests seemed to indicate that lithium could be detected using primary absorption (detection of natural spectra unassisted by reagents), subsequent field tests demonstrated that no primary absorption spectra existed for lithium in the ultraviolet-visible wavelength range. A second series of tests that were recently conducted did, however, confirm results reported in the literature to the effect that reagents were available that will react with lithium to form chelates that possess detectable absorption and fluorescent signatures. These results point to the possible use of secondary techniques for on-line analysis of lithium.

Introduction

Approximately 75% of the total area exposed to the primary coolant in a Pressurized Water Reactor (PWR) is in the form of alloy 600 tubing. EPRI has noted that the major sources of radiation fields in PWRs are a result of the release of cobalt and nickel from alloy 600 in the corrosion process and deposition of corrosion products onto fuel surfaces, where activation products such as ^{58}Co and ^{60}Co are formed. The activation products are gradually released back to the coolant and circulated in soluble, insoluble and colloidal forms, such that the subsequent deposits on system surfaces result in the buildup of radiation fields.[1]

In a PWR system, rigid controls are required for reactor coolant chemistry, including optimum levels of boric acid and lithium hydroxide to absorb excess neutrons and control pH. The emphasis on corrosion control is to assure component integrity but also to minimize shutdown radiation levels. Data on corrosion of alloy 600 indicate that corrosion rates are lower at higher pH levels. Additionally, variations in pH have been shown to affect the solubility and transport of corrosion products. Several studies have shown that there is a basis for maintaining lithium concentrations at a level that provides a constant pH of at least 6.9 (or higher) at 300 C for any given boron concentration.

In order to maintain constant pH, the lithium levels must be altered when boron concentrations have been changed. Boric acid concentrations are frequently varied to compensate for fuel consumption and to control reactor power. This requires frequent analysis of lithium levels in the reactor coolant in order to maintain a constant optimum pH. Current practice is to subject a daily grab sample to analysis using Atomic Absorption Spectrometry, but such a practice may not provide as close a degree of control as is necessary, especially at plants that practice load following.

An ideal monitoring instrument for reactor coolant pH control would yield highly sensitive, accurate and precise measurements of lithium concentrations directly in the reactor coolant and would do this continuously and automatically, without the need to extract and process samples. Such an instrument could eventually be linked to

the appropriate control systems, so that optimum pH could be automatically maintained. If such an instrument could also simultaneously perform on-line analysis of boron concentrations, this capability would also be highly desired.

Ultraviolet-visible absorption spectrometry (UVAS) has been suggested as one instrument technology that is capable of providing the kind of dependable analytical results required for on-line monitoring of lithium in reactor coolants. This is because UVAS can operate through fiber optic probes which can be located directly in a hostile environment (resulting from pressure, temperature and radiation), while the instrument itself can be located in a nearby benign environment. Since only light energy is transmitted between the analyzer and the optical probe, handling of radioactive samples for lithium analysis can be eliminated, which minimizes the need to dispose of radioactive waste products after analysis.

INITIAL ABSORPTION SPECTROMETRY EXPERIMENTS

The objective of using UVAS for continuous on-line analysis of lithium is only practical if lithium has primary (natural) or secondary (chemically induced) absorption spectra in the ultraviolet-visible wavelength range (200 nm to 800 nm) of sufficient character and intensity for detection using an on-line ultraviolet-visible absorption spectrometer.

In August of 1990, Wisconsin Electric Power Company prepared a Box-Behnken set of standards containing 13 varied non-radioactive concentrations of lithium, boron and ammonia for use at Biotronics to characterize absorption spectra and process a learning set that would help select the most appropriate analysis algorithms for spectrometric measurements. One of the standards contained a known concentration of lithium but no concentrations of either boron or ammonia. This standard was used to identify and characterize any absorption spectra that might have existed for lithium. The research team that conducted the experiments at Biotronics did not expect to find primary absorption spectra for lithium since the electron structure of alkali metals were not known to be easily excited by the relatively low energy available in the ultraviolet-visible wavelength range.

Ten of the standards were processed as a learning set and three of the standards were held for later use as a test set. To the surprise of the team, the lithium standards that were processed exhibited strong absorption characteristics in the 190 nm to 240 nm range. These tests were conducted using a laboratory Perkin Elmer Lambda 9 UV-VIS Absorption Spectrometer, which compares a static sample in a quartz cuvette using a 10 mm path length with a reference standard of pure water in a second cuvette at the same path length. Seven of the standards in the learning set had an identical concentration of lithium (1.55 ppm), but different concentrations of boron and ammonia. This subset included the standard that had no boron or ammonia concentrations. The spectra detected for each standard in the subset was nearly identical, as seen in Figure 1.
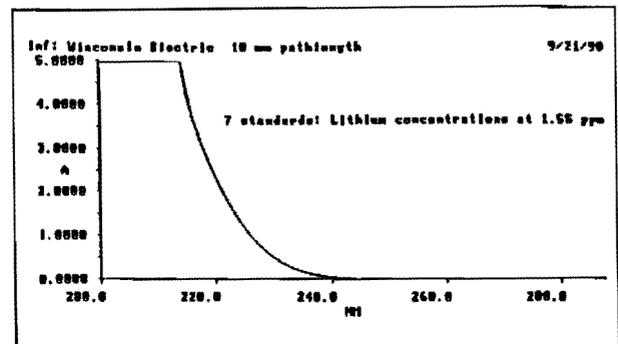

Figure 1. Spectra from seven standards.

Distinct and repeatable patterns were observed for each of the three lithium concentrations in the experiment (0.10 ppm, 1.55 ppm and 3.00 ppm) regardless of the variation in either boron or ammonia levels. This can be seen in Figure 2 which shows the typical spectra detected for each of the three concentrations. Given this distinct pattern, the use of discriminant analysis techniques had little difficulty in appropriately matching a detected spectra for test set standards into the appropriate class with other spectra from standards that had the same lithium concentration.
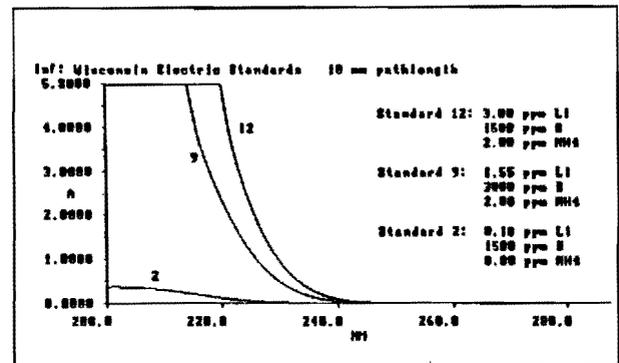

Figure 2. Absorption spectra at three Li concentrations.

Discriminant analysis might be appropriate if the analysis task were limited to classification of unknowns into several well separated groups, but the anticipated application calls for continuous measurement of variable lithium concentrations within a known operating range (1.9 to 2.2 ppm typical), an analytical task which requires a fair degree of precision. Therefore, an analytical method was evaluated that could provide predictions of lithium concentrations, within the boundaries of the learning set, with the lowest possible standard error of prediction (S.E.P.). Although a number of advanced techniques were available for the analysis (first or second derivatives, Fourier or Walsh transformation, principal component analysis, etc.) an excellent S.E.P. of 0.009 ppm was obtained in the learning set using simple stepwise regression of untransformed absorbance values.

LABORATORY EXPERIMENTS USING AN ON-LINE SPECTROMETER

In early 1991, a similar set of standards were obtained' from Wisconsin Electric for the purpose of determining if the results that were obtained on the laboratory instrument could be duplicated using an analyzer that had been developed at Biotronics specifically for the purpose of performing on-line ultraviolet-visible absorption spectrometry using optical probes linked to the analyzer with fiber optic cables. A sketch of a typical flow-through optical probe is shown in Figure 3.
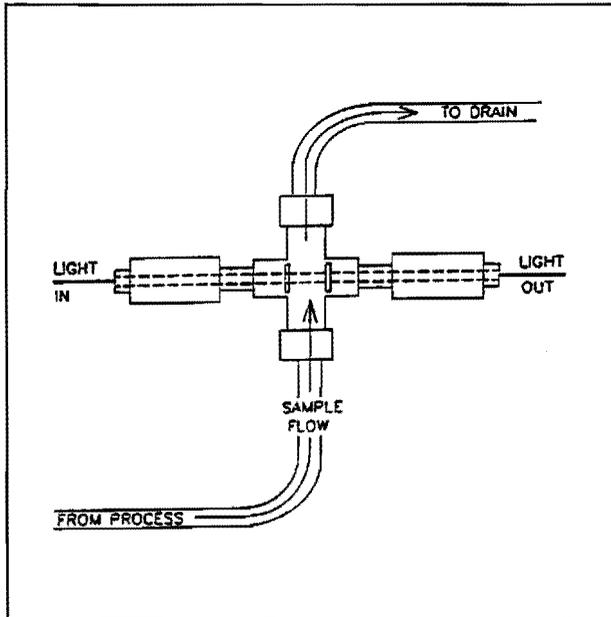

Figure 3. Flow through optical probe.

Tests were conducted at Biotronics in January 1991 using non-radioactive samples furnished by Wisconsin Electric. An apparatus was constructed that allowed use of the flow through optical probe for sequential batch processing of standards that were manually poured into the probe, scanned for absorption spectra, then allowed to drain. The probe was then flushed with pure water until zeroed, after which the next standard would be processed. A learning set consisting of 12 standards were processed using the described techniques to obtain an information base for analysis using regression of raw absorption values, as was done with the standards previously processed on the laboratory instrument. This analysis produced an S.E.P. comparable to the results obtained with the laboratory instrument. Test set sample concentrations ranging from 0.90 ppm to 2.10 ppm were measured with an S.E.P. of 0.005 ppm, which was considered to be well within the desired precision for the experiment. Figure 4 shows a photograph of the optical probe and analyzer used for these experiments.

Figure 4. Optical probe and analyzer in use.

The on-line analyzer contains a xenon flash lamp for excitation across the entire ultraviolet-visible range. Light is introduced to the sample using a 3.5 meter length of fiber cable running between the analyzer and the optical probe. A companion fiber cable of equal length is used to return the light remaining after absorption to the analyzer for detection in a spectrograph that includes a fixed diffraction grating and a 1024 element photodiode array detector. Any spectra detected over the range scanned (200 nm to 800 nm) is recorded and available for analysis using chemometric pattern recognition techniques. Figure 5 shows a block diagram of this analyzer.
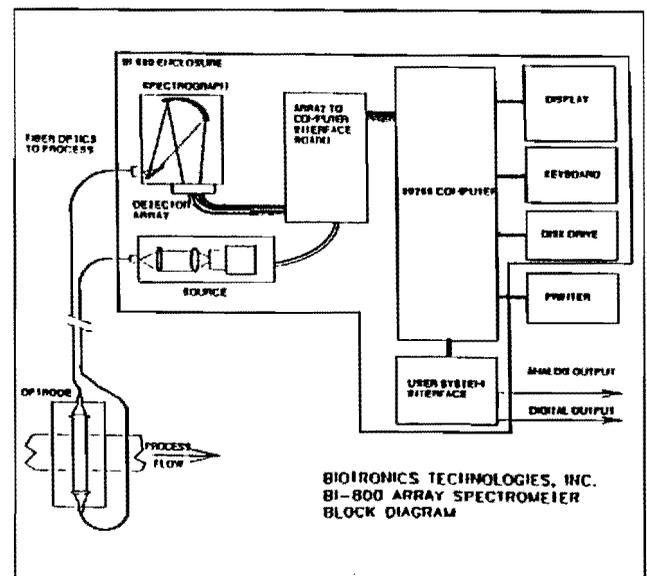

Figure 5. Array Spectrometer Block Diagram.

FIELD TESTS USING THE ON-LINE SPECTROMETER

Because the lithium analysis results obtained with the on-line instrument through the remote optical probe were comparable to the lithium analysis results from the laboratory instrument, the research team believed that a field test at the Wisconsin Electric Point Beach Nuclear Plant was a logical next step. Field tests were conducted in early February 1991.

Field tests were divided into two phases. The first phase included the processing of a series of non-radioactive standards with known lithium concentrations and a random background of boron and ammonia concentrations. Information from the learning set would be used to predict lithium levels in samples that were extracted from the reactor coolant during the second phase of the tests. The same "pour through" optical probe that was used in the previous tests at Biotronics was used for the field tests at Wisconsin Electric. The analyzer was programmed to process information using the same analytical technique as prior experiments, regression of raw absorption spectra. After an initial warm-up period, standards were introduced into the probe by Wisconsin Electric personnel.

Although the analyzer required some adjustment for drift that occurred across the entire range of lithium standards processed (the drift was approximately 0.10 ppm over the range of 0.10 ppm to 6.66 ppm), the analyzer was able to produce enough precision in the learning set to permit the experiment to proceed to the second phase. Primary reactor coolant samples with unknown lithium concentrations were extracted and split for analysis using ultraviolet-visible absorption spectrometry and conventional AA methods so that the relative accuracy of the two methods could be compared.

The primary reactor coolant sample was introduced into the optical probe by Wisconsin Electric personnel and scanned for absorption spectra. NO DETECTABLE ABSORPTION SPECTRUM WAS OBTAINED FROM THIS SAMPLE. The split portion of the sample that was analyzed using conventional methods did indicate that the sample DID contain a concentration of lithium that was within the range of the learning set and should have been able to be detected in the sample. Several repeats of the analysis demonstrated identical results, leaving researchers with the question of why spectra were able to be detected in all of the non-radioactive samples but not in the sample from the reactor coolant.

An answer was provided when the chemistry of the laboratory standard used in the experiments was examined. All "non-radioactive" standards that were prepared used a laboratory grade lithium standard that contained trace levels of nitric acid to stabilize the standard. Nitrates would therefore appear in all of the prepared lithium/boron/ammonia standards in exact proportion to the concentration of lithium that was intended to be present in each standard. Nitrates exhibit strong absorption spectra in the 200 nm to 240 nm range. This would explain why the analysis of "lithium" was so precise in the learning sets even though no lithium was able to be detected in the real sample. The lithium that appears in the reactor sample was originally introduced in the form of pure lithium hydroxide in the reactor water. No nitrates are present. The conclusion of this series of experiments was that the analytes of interest (lithium and boron) did not possess any natural absorption spectra in the ultraviolet-visible range.

SECONDARY ABSORPTION EXPERIMENTS

Although the nitrate explanation answered the question of why primary absorption spectra were detected in the laboratory, the research team was still left with the original problem of finding a technique that could be used for reliable on-line detection of lithium directly in the reactor coolant environment. With the elimination of primary UVAS techniques, attention shifted to so called "secondary" techniques. These secondary techniques make use of reagents that will selectively form chelates with the analyte of interest and have distinct absorption or fluorescent signatures.

A literature search revealed that 8-hydroxyquinoline and its derivatives form intensely fluorescent chelates with lithium.[2] Since fluorescence is essentially a return of energy from an excited state to a ground state, the absorption of the energy that caused the original excitation will be able to be detected as an absorption spectra at wavelengths lower than the fluorescent spectra. The research team has had prior experience working with 8-hydroxyquinoline (abbreviated as 8-OH-Q) as a reagent for magnesium in nutrient solutions, under NASA sponsorship.[3]

A series of experiments were conducted at Biotronics during April and May of 1991 in order to confirm that chelates formed by lithium and 8-OH-Q would produce detectable and predictable absorption spectra.

In the first series of experiments, a saturated solution of 8-OH-Q was spiked with standard lithium solutions (prepared from LiOH standards free of nitrates) to create eight concentrations ranging from 0.13 ppm to 6.66 ppm. Over the range of 0.13 ppm to 0.60 ppm, the amount of absorption at 375 nm DECREASED as the concentration of lithium was increased. This is consistent with the typical pattern seen when the analyte quenches the natural absorption spectra of the reagent. At concentrations of 1.30 ppm and above, however, the pattern is reversed. An INCREASED intensity of absorption is observed. It is unusual for absorption intensity to decrease and then increase at a given wavelength over a range of sample concentrations. These results are summarized in Figure 6.
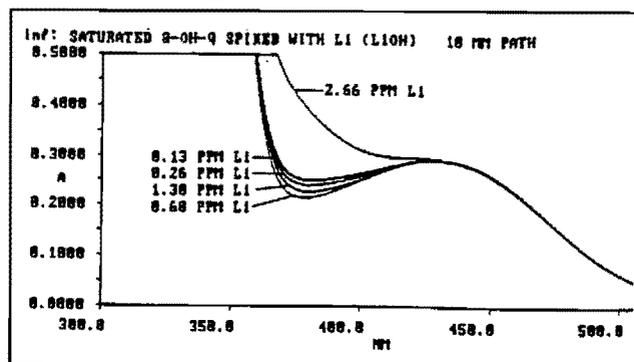

Figure 6. Selected spectra, lithium with 8-OH-Q

A second series of experiments were conducted with 12 lithium concentrations from 0.13 ppm to 6.66 ppm, including all concentrations identical to those in the first experiment. The same saturated concentration of 8-OH-Q was used. Results from the second series of experiments were identical to the first, with a range of decreasing absorbances at low concentrations, converting to increasing absorbances at concentrations of 1.30 ppm and above. In both experiments, 0.60 ppm lithium represented the lowest absorbance intensity at 375 nm. Figure 7 shows absorbance spectra from this series of experiments.
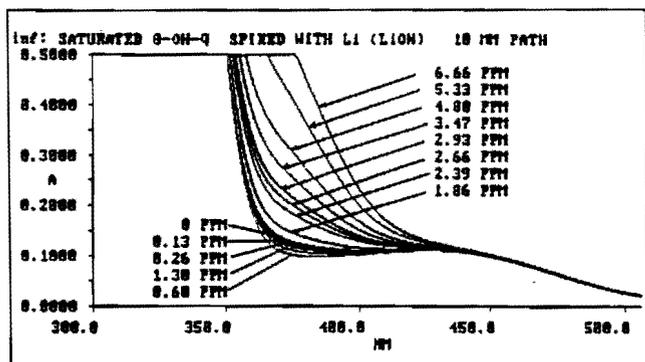

Figure 7. Second experiment, lithium with 8-OH-Q

Another series of experiments were conducted, this series using a more dilute solution of 8-OH-Q (25% of the concentrations used in the first two series). It was hypothesized that if an interfering component that preferentially reacted with 8-OH-Q were present, there should be a shift in the concentrations at which a crossover from decreasing to increasing absorbance could be observed. Instead, the reduction in 8-OH-Q concentration allowed additional absorption spectra detail to be detected in wavelength regions that had been previously saturated at higher reagent concentrations. Although an additional crossover could now be observed at approximately 270 nm, the 0.60 ppm sample still exhibited the lowest absorption in the decreasing bands and the highest in the increasing band. Spectra can be seen in Figure 8. The absorbance values, not yet processed using any pattern recognition technique, appear to be very linear and predictable in the 1.30 ppm to 6.66 ppm concentration ranges.
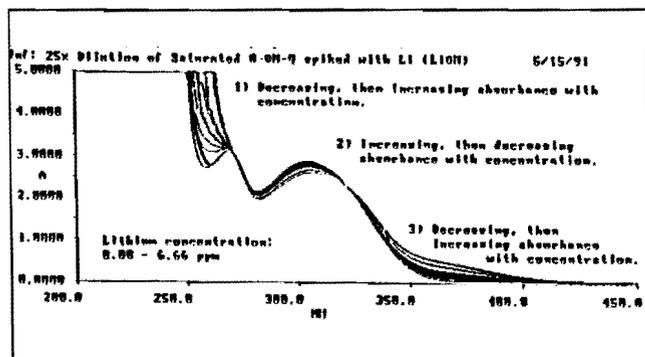

Figure 8. Experiment using dilute 8-OH-Q concentration

OBSERVATIONS AND CONCLUSIONS

One of two conceptual approaches could be used for on-line analysis. Although it would be undesirable and uneconomical to introduce a reagent into the primary coolant merely to provide some means for detection, it would be possible to inject a controlled amount of reagent into a side stream sample extracted from the coolant. The treated sample could be fed through a flow cell optical probe, detected, then discarded. This technique could be employed continuously, at scheduled intervals or on-demand. In any case, some quantity of radioactive waste is created and an available supply of the reagent is required, both disadvantages for the flow injection concept.

The other conceptual approach is to immobilize the reagent on a substrate that can be mounted in the optical cell or directly on the optical fiber. As the sample stream flows past the substrate, chelate density increases or decreases in proportion to the concentration of analyte in the flow. This can be optically detected using absorption or fluorescent spectrometry. For this to be a practical alternative, methods need to be found to immobilize the reagent on a transparent substrate (for transmissive analysis) or opaque substrate (for reflective analysis). Thus, an important objective for this method is to verify that the reagent and immobilization technique will produce a proportionate reversible reaction with lithium that is confined to the surface of the substrate or fiber cable. Similar immobilized reagent techniques are currently in successful use on other types of fiber optic sensors and for other analytical applications.

One possible impediment for either approach is the possibility of interferences from other chemical constituents that may be present in aqueous solutions, although it may be possible to find a derivative of 8-OH-Q that resists such interference. Iron, calcium, magnesium, aluminum and zinc are all known to react with 8-OH-Q requiring that the water be free from any substantial concentrations of these chemical substances. Fortunately, the proposed application is for analysis of a reactor coolant water that has been purified using an ion exchange process. This reduces the concentration of ionic impurities to less than a few parts per billion, well under the point where interference from any of these impurities would be a significant concern.

The on-line spectrometer that was used for the field tests in this study was a prototype instrument. Drift in the instrument that was noted in this study was attributed to the fact that this is a single beam instrument. The software that corrects for drift and other non spectral perturbations through the use of one or more reference wavelengths was not functioning. This has since been corrected. In future applications, one or more reference wavelengths in the 200 to 800 nm range that are not affected by any of the components in the matrix under investigation will need to be selected and continuously compared to lamp output. This not only corrects for drift, but also eliminates other sources of error such as light scattering, film on optical probe windows, etc.

We conclude that secondary absorption appears to be a candidate technology for on-line lithium analysis,

especially at concentrations of 1.3 ppm and higher. Since the typical control range for lithium is 1.9 to 2.2 ppm, secondary absorption appears to be a good candidate for routine control use under normal conditions. Lithium concentrations may, however, be reduced to maintain constant pH as Boron concentrations are reduced. Since control of lithium at concentrations of as little as 0.2 ppm may be necessary, more laboratory experimentation is required for the concentration ranges below 1.3 ppm. Also, a study of more dilute reagent concentrations may reveal additional useful information at wavelengths below 250 nm. Increased pathlengths may improve resolution. Chemometric pattern recognition algorithms will need to be developed and tested for analysis of unknown concentrations. The laboratory results will need to be verified on actual reactor coolant samples. A literature search indicates that several reagents are available for boron analysis using absorption or fluorescence. Use of these reagents for analysis of boron concentrations need to be explored. In addition, practical and economical techniques will need to be found to support either flow injection or immobilization of the reagents for on-line use.

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