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AUTOMATED PROCEDURE FOR ZIRCONIUM ANALYSIS IN WATER⁽¹⁾

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OUTLINE

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INTRODUCTION

Zirconium and zirconium alloys are used extensively for pressure tubes and fuel element cladding in water-cooled nuclear reactors because these materials have relatively high corrosion resistance and low neutron absorption characteristics. However, under some conditions these materials are susceptible to an accelerated type of corrosion called "fretting" which is generally attributed to vibration induced wear damage.

A [REDACTED] program is being conducted at the Pacific Northwest Laboratory to identify the conditions that promote fretting attack and to develop effective methods for minimizing their effects. One phase of this effort is directed toward developing an accurate and reliable method to monitor the trace amounts of zirconium present in the reactor coolant streams.

APPLICATION

The zirconium concentration normally present in the coolant streams is less than 1 ppb, but when fretting occurs the concentration can increase rapidly to 10 ppb or more.⁽¹⁾ Thus a satisfactory zirconium analysis procedure for detecting the occurrence of fretting must have a sensitivity of at least 1 ppb and a reproducibility of about ± 0.5 ppb. Instrument response time is not critical for this application, since a sampling frequency as low as three times per hour should be satisfactory.

PREVIOUS WORK

Present manual procedures for zirconium analysis in the concentration range of interest generally involve spectrographic techniques preceded by an evaporative concentration step. Such procedures are not suitable for our purposes due to the relatively long analysis time required per sample even if the procedures could be automated. The Russians have reported success with colorimetric analysis procedures using Arsenazo III as the indicator in a HCl reaction medium.⁽²⁾ Unfortunately our attempts to automate their procedure were unsuccessful, since we were unable to obtain the reported sensitivity and the reproducibility was quite poor. Similar investigations in our laboratory using Morin as the indicator were also unsuccessful in developing a suitable procedure.

At the present time we are devoting our efforts toward automating a manual fluorescence analysis procedure developed by Geiger and Sandell.⁽³⁾ Our work on this procedure is not yet complete, thus this paper is only intended to summarize the present status and direction of the investigation.

CHEMISTRY

The procedure developed by Geiger and Sandell in essence involves a differential fluorescence technique. It employs Morin as the indicator in a HCl medium and relates the solution differential fluorescence before and after addition of di-sodium ethylenediammine tetraacetic acid (Na_2EDTA) to the zirconium

concentration. The great utility of the procedure lies in the fact that it can make use of the relatively high specific fluorescence of the Zr:Morin complex while simultaneously eliminating the interference effect of other materials that may be present in the sample stream (e.g., Al, Sb, Th, and U).

We automated this differential fluorescence technique for use with a conventional AutoAnalyzer unit with a fluorometer detection module as shown by the schematic diagram on Figure 1.

After the Morin is added to the sample, mixed, and given time to react, water is added and the resultant solution is mixed prior to measuring the solution fluorescence. Approximately ten minutes after the sample starts through the analysis cycle a 3-way solenoid valve repositions and Na_2EDTA is injected in the mixed sample-plus-Morin solution in place of the water added initially. A second fluorescence value is thus obtained for the same sample. When the 3-way valve repositions the sample stream selector simultaneously advances to the next position to provide a new sample and the analysis cycle repeats.

The solutions employed for this analysis are prepared as follows;

Morin

Dissolve 90 milligrams of reagent-grade Morin in a solution prepared by mixing 70 milliliters of deionized water and 290 milliliters of absolute ethanol. This solution is stable for several weeks.

METHOD: ZIRCONIUM

REFERENCE: GEIGER AND SANDELL, ANAL. CHIM. ACTA, VOL.16, P.346 (1957)

RANGE: 0-100 PPB

DATE: JANUARY 6, 1965

AUTHOR: THOMAS F. DEMITT

AFFILIATION: BATTELLE-NORTHWEST

Na₂EDTA

Dissolve 7.15 grams of reagent-grade Na₂EDTA in one liter of deionized water. This solution is stable indefinitely.

These preparative procedures are designed to provide the same molar reagent concentrations used by Geiger and Sandell consistent with the flow rates used in our automated procedure.

RESULTS

Our studies to date have been performed almost entirely with standard solutions of zirconium oxychloride (ZrOCl₂) in HCl, and have been devoted to determining the sensitivity and reproducibility of the procedure. Since no significant amounts of impurities are present in our standard solutions, the use of Na₂EDTA to quench the fluorescence of impurities has not been necessary. We have, however, conducted preliminary experiments to confirm that this technique is suitable for eliminating the interference effect of aluminum which is the major impurity present in the reactor coolant streams of interest to us. No significant problems are anticipated from other impurities likely to be encountered. This brief commentary concerning the Na₂EDTA portion of the procedure is all the information I have available on this subject at the present time. The balance of the discussion concerns the results obtained with the pure zirconium standard solutions.

The most troublesome problem associated with the measurement of zirconium in aqueous solution is hydrolysis which converts the

zirconium to forms (oxides and hydroxides primarily) which are difficult to detect. The most expedient method for minimizing the hydrolysis reactions is to acidify the solution with HCl. Our results indicate that a 2-4 M HCl environment is satisfactory and variations in acid concentration within this range are not critical. We have standardized on the use of 4 M HCl for preparation of all stock and working standard solutions.

Using the reagents and procedure described previously, we obtained the calibration curve shown on Figure 2. This curve was obtained using a Fluorometer signal expansion factor of 30X and a recorder range expansion factor of 1X. Note that additional sensitivity can be obtained easily by increasing the recorder range expansion; thus we are confident that sensitivity will not be a major problem with this procedure.

However, as the calibration curve clearly shows, our major problem is lack of reproducibility for readings obtained from the same sample. This problem could be caused by a non-homogeneous sample solution or by problems inherent in the analysis flow scheme. The increased reproducibility of the higher concentration samples indicates that inhomogeneity of the sample solutions is not likely. Attempts are therefore being made to improve both the chemistry of the procedure and the mechanics of the analysis system.

Chemistry

Scanning tests demonstrated that variations in reaction time before and after adding water to the Zr:Morin complex, and

FIGURE 2 - Calibration Curve For Zirconium In Water

variations in Morin concentration do not improve the data reproducibility. Variations in the ethanol concentration of the Morin reagent cause changes in both sensitivity and in reproducibility, and results in this area are not yet conclusive. However, it is considered unlikely that significant improvement will result from optimization of this variable. The next variable scheduled for evaluation is Morin purity. Morin from several sources as well as repurified reagent will be evaluated for possible effects on data reproducibility.

Analysis System

The fluorometer module used in these studies is currently being adapted to utilize a larger flow cell, and lamp bulbs that emit a higher proportion of radiation at the excitation wavelength have been obtained. The effect of these changes on procedure sensitivity and reproducibility will be evaluated in the near future.

SUMMARY

A simple and effective technique for automating differential fluorescence analysis procedures was developed. The technique was used to adapt an existing manual procedure for zirconium analysis in water for continuous operation. Although the procedure has not been optimized and the ultimate sensitivity and reproducibility have not been determined yet, it is apparent that it can be used to monitor zirconium concentrations in the ppb range. The procedure may eventually be suitable for detecting accelerated corrosion of zirconium and zirconium alloys in water environments.

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3. Geiger, R. H., and E. B. Sandell, "Fluorimetric Determination Of Zirconium With Morin," Anal. Chim. Acta, 16:346, 1957.