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AUTOMATED PROCEDURE FOR H_3BO_3 ANALYSIS IN WATER⁽¹⁾

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AUTOMATED PROCEDURE FOR H_3BO_3 ANALYSIS IN WATER⁽¹⁾

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AUTOMATED PROCEDURE FOR H_3BO_3 ANALYSIS IN WATER

INTRODUCTION

Most nuclear reactors utilize neutron "poisons" to control the fission chain-reactions. These poisons are materials that absorb some of the free neutrons within the reactor core without contributing to the propagation of the fission reactions. The poison materials may be solid objects which can be inserted or withdrawn to vary the neutron absorption rate, or they may be dissolved in the liquids that circulate within the core in which case the poison concentration must be varied to control the neutron absorption rate.

Boric acid is one of the materials that can be used as a dissolved poisoning agent and is being investigated for use in the Plutonium Recycle Test Reactor (PRTR), Richland, Washington. This reactor is operated to develop technology for utilizing plutonium as a nuclear fuel material to promote the peaceful use of atomic energy.

APPLICATION

The boron concentration range initially of interest for the PRTR application is 0-10 ppm, although ultimately a higher range may be needed. The operating conditions are such that the boron concentration must be continuously monitored to provide information necessary to control the boron concentration. Additional requirements include a maximum instrument response time of 5 minutes to facilitate monitoring several sampling points, a sensitivity of 0.1 ppm, and a reproducibility of ± 0.2 ppm in the 0-10 ppm boron range.

PREVIOUS WORK

Analytical procedures for boron in water have been studied by several investigators and in general include volumetric, spectrometric, and colorimetric techniques. The methodology recommended by Technicon Controls, Inc., is an adaptation of the manual procedure described by Snell and Snell,⁽¹⁾ and involves measurement of the colored reaction product formed when boron reacts with carminic acid in a concentrated H_2SO_4 medium. Excellent results can be obtained using this procedure; however, for on-line monitoring applications rather elaborate precautions must be taken to protect both the instrument and service personnel from the aggressive action of the H_2SO_4 if failure of the solution containment system occurs (e.g., rupture of pump tubing, failure of a tubing-to-fitting joint, etc.). A further disadvantage of the procedure from our standpoint is the relatively long response time (~ 15 minutes) required to obtain stable sample readings. Although response time could probably be reduced somewhat by modifying the flow cell design, we felt that the high viscosity of the H_2SO_4 would cause fluid drag problems in the tubing and time delay coils that might prevent achieving the relatively rapid response we desired.

BATTELLE-NORTHWEST H_3BO_3 ANALYSIS PROCEDURE

We therefore directed our efforts to developing an alternate colorimetric analysis procedure. Scanning tests with carminic acid and quinalizarin reagents in aqueous (rather than acid) solutions quickly verified previous reports that these reagents are not

effective under these conditions. We then began investigating basic reaction mediums and found that a satisfactory procedure could be developed using carminic acid reagent under these conditions.

In essence the procedure developed involves buffering the sample stream with $\text{NH}_4\text{Cl} - \text{NH}_4\text{OH}$ solution and then adding a small amount of an aqueous solution of carminic acid. In the absence of H_3BO_3 the amount of blue neutralization product formed is directly proportional to the amount of carminic acid present (actually this step could be the basis for a carminic acid analysis procedure). When H_3BO_3 is present, it reacts with the neutralized carminic acid resulting in decolorization. The amount of decolorization is directly proportional to the boron concentration present. Our process thus involves two separate colorimetric processes with the actual controlling factor involving measurement of the indicator rather than the H_3BO_3 concentration.

A methodology flow sheet illustrating our procedure is shown on Figure 1. Note that transmittance measurements are made at 575 millimicrons and that we employ a multi-pass (~ 47 millimeter light-path) flow cell. With the system arrangement and flow rates shown, the instrument response time is about 4.5 minutes. This could probably be reduced somewhat if required by increasing liquid flow rates or by using a smaller time delay coil.

The buffer solution indicated is 4 M NH_4Cl and 1M NH_4OH . The carminic acid solution is prepared by adding 0.2 grams of the reagent

METHOD: BORON

REFERENCES: NONE (ORIGINAL PROCEDURE)

RANGE: 0-30 PPM

DATE: JANUARY 6, 1965

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to a liter of deionized water, stirring overnight, and then filtering to remove the solid residue. Both reagents are stable for at least 4 weeks.

Perhaps preparation of the carminic acid solution could be simplified by first dissolving the reagent crystals in alcohol and then diluting to the required concentration with deionized water. While we know this will eliminate the necessity for filtering the solution, we have not yet determined whether it would be suitable for use in this analysis procedure.

Typical calibration charts for solutions of H_3BO_3 in deionized water are shown on Figure 2. The desired sensitivity of 0.1 ppm B can be obtained using 10x range expansion. The reproducibility is within the ± 0.2 ppm limit for average peak readings, although peak-to-peak noise level values occasionally give indications of ± 0.4 ppm at high signal amplification.

We evaluated the effect of various impurities on this procedure and found no measurable deviation due to ppm quantities of the halides or alkali metals unless acids or hydroxides were added that changed the pH of the buffered system. Metals that form insoluble hydroxides in the pH 8.6-8.7 buffered solutions interfere - especially aluminum. Copper interferes slightly due to formation of a copper-ammonia complex. Tests conducted with samples from the high-purity water from PRTR revealed no interference effect from the impurities present in this system.

FIGURE 2 - Calibration Curves For Boron In Water
(Carminic Acid = 0.2 grams/liter)

ON-LINE OPERATION

The major problem we faced in adapting the laboratory procedure for on-line operation was the effect of pressure variations in the sampling system. Since our procedure in essence involves measurement of variations in the reagent concentration, it is extremely sensitive to any variation in the reagent stream flow rate through the proportioning pump. Since variations in sample stream inlet pressure can cause slight variations in the reagent flow rate, it was necessary to design a sample handling system to provide a constant pressure sample source. Although a simple overflow sampling device downstream of the sample stream selection system would appear satisfactory for this application it presented significant problems in controlling the individual flow rates from our various sample points where pressure variations range from 0 to about 95 psig, and with controlling the spread of radioactive tritium gas present in the sample streams.

We finally selected a modification of the overflow sampling system to meet our application needs. This system is shown on Figure 3. Basically we employ a conventional solenoid valve operated sample stream selector, a constant volume displacement pump to meter solution flow and to elevate the discharge pressure to a value slightly above that of the highest sample stream pressure, a pressure control valve to regulate pump discharge pressure, and an overflow sampling unit to provide feed to the AutoAnalyzer sampling pump. Since the metering pump stroke length can be adjusted to supply a

FIGURE 3 - Schematic Diagram Of On-Line H_3BO_3 Sampling System At PRTR.

sample stream flow rate just slightly greater than the flow rate through the AutoAnalyzer pump, this system minimizes the amount of sample required for analysis. The closed sample handling system also minimizes release of tritium gas to the atmosphere.

SUMMARY

An original inverse colorimetric analysis procedure was developed, and an automated sample handling system was designed, to permit continuous measurement of trace concentrations of H_3BO_3 in water. The integrated system has been used for on-line monitoring of H_3BO_3 in the Plutonium Recycle Test Reactor moderator under actual process conditions. The results obtained confirmed the suitability of the sample handling and analysis techniques employed. We feel that this system has significant response time and safety advantages over other published procedures for this application.

REFERENCE

1. Snell, F. D., and Snell, C. F., Colorimetric Methods Of Analysis, Volume IIA, D. Van Nostrand Co., Inc., New York, 1959, p. 595.