Summary

The papers in this book have been arranged in the following order: (1) the panel discussion, (2) general guidelines and requirements for monitoring high-purity water, and (3) presentations of the newer techniques and applications of monitoring by ion chromatography, atomic absorption spectrometry, specific-ion electrodes, ion-exchange columns, electrical conductivity, a gravimetric technique, and differential pulse polarography. Particular attention has been directed toward the development of on-line instruments that provide continuous measurement by these techniques. The importance of proper sampling techniques, where to sample, sample bottle materials, the preparation of sample bottles, preservation of the samples, and the necessary care and handling of samples have also been emphasized.

J. K. Rice, the introductory session chairman, and the panelists, F. J. Pocock, O. Jonas, T. C. Hoppe, and J. Brown, have discussed the history of the measurement of the quality of high-purity water, the measurement methods now available for measuring the quality of higher-purity water, and the need for continuous on-line instrumentation to provide the chemical control needed in monitoring all volatile types of treatment in the modern high-pressure power plant. The meticulous care and the difficulties involved in measuring 1-ppb levels of impurities have been emphasized. The importance of measuring and minimizing the Cl^- and $SO_4^=$ ingress into the system and the need for monitoring the total organic carbon have been discussed. The need for continuous analyses plus grab sampling of condensate and steam, and the difficulties of sampling properly, choosing the points of sampling, investigating the transfer of corrosion products in the system, and assessing and developing correlation of the collected data have all been given attention. At Ontario Hydro (Toronto, Canada), concentrations of corrosion products were determined by analyzing samples collected on Millipore filters and cation resin–impregnated paper. It was also reported that valveless capillary samplers acted as both sampling probes and pressure reducers to provide unbiased samples of feedwater particulates.

Noll has pointed out that the chemical concentrations allowed in the steam–water cycle are dictated by the low levels specified for the turbine and that the specifications for boiler water, feedwater, condensate, and makeup water then fall in line in logical sequence. Measurements of pH, sodium, and cation conductivity, however, are considered essential. Noll also presented a chart showing the most sensitive monitoring scheme for monitoring cooling water inleakage. The choice of monitoring Na^+, silicon dioxide, or cation

conductivity was observed to be dependent on the analysis of the cooling water.

Selby has emphasized the need for proper power plant organizational structure and educational requirements for plant chemists in order to attain reliable maintenance and calibration of water quality instrumentation. His data indicate that plants delegating the responsibility of operating and maintaining this instrumentation for water quality control to those responsible for plant chemistry functions had fewer problems with instrumentation and with chemical control.

Pensenstadler, Peterson, Bellows, and Hickam have reported on their 3-year program in six fossil fuel plants, in which thorough studies of the steam-turbine chemical environment and the determination of the source of corrodent species were conducted. This program included the development and application of a continuous on-line analyzer for determining Na^+, oxygen, pH, cation conductivity, and specific conductivity. The steam sample supplied to this analyzer was a cooled, continuously flowing sample taken from a well-designed sampling nozzle in the crossover piping between the intermediate and low-pressure turbines. This point of sampling was chosen because turbine deposits and turbine cracking have been generally observed in this area. In addition, a grab sampling program was simultaneously conducted as a total plant survey, in which samples were taken at multiple locations and submitted to ion chromatography analysis. Although the quality of steam from plants experiencing turbine attack was observed to be within the recommended ranges of Na^+ and cation conductivity most of the time, steam from plants not experiencing turbine attack was generally of higher purity and provided larger margins for error. At some plants high cation conductivity indicated appreciable air inleakage; however, it was observed that it is not known at this time whether such air inleakage is a factor in the general corrosion problem. It was reported that cation conductivity was a better indication of the likelihood of turbine corrosion than the Na^+ determination.

Willhite, Sawochka, and Pearl have demonstrated that cumulative sampling in cation and anion ion-exchange columns for periods of 6500 min provided indicative results for Na^+, Cl^-, and $SO_4^=$ from eleven sample points in nuclear plant studies. There was relatively good agreement between specific ion-electrode results for Na^+ and ion chromatography results for $SO_4^=$ during short-term studies. The sample collection system also included a Millipore 0.45-μm membrane for collecting filterable species before they reached the cation and anion resin columns.

Rawa has observed that there had previously been no accurate method for measuring trace concentrations of anionic constituents but that the new analytical technique of ion chromatography provides a means of identifying and quantifying the anions Cl^-, NO_3^-, $PO_4^=$ and $SO_4^=$ at microgram-per-litre levels. The levels of detection are improved approximately a hundredfold by the concentrator column technique.

Girard and Glatz have reported that a nonsuppressed ion chromatography technique offers a new alternative method which avoids the need for a suppressor column and regeneration of said column. The sensitivity to Cl^-, NO_3^-, and $SO_4^=$ in this technique is nearly equal to that in the conventional technique.

Simpson, Robles, and Passell have reported the development of an on-line instrument employing ion chromatography for measuring anions and cations at microgram-per-litre levels in an electric generating plant. This development also includes an on-line sampling and calibration system.

Diggens has advised that while specific-ion electrode technology has been used successfully in laboratory measurement for many years, recent developments in which these electrodes are less complex and more reliable are proving that this measurement technique, particularly for sodium, is one of the most reliable and useful in the modern power plant. Other electrodes for Cl^-, chlorine, Ca^{++}, $SO_3^=$, and $S^=$ are reported to be accurate in the microgram-per-litre range.

Eherts has reported that he has not found the results obtained with Na^+ ion analyzers to agree well with the actual system concentration variance obtained by atomic absorption spectrometry or ion chromatography. His experience indicates that this measurement should be restricted to systems characterized by low solids content and that the nonrepresentative variations observed correlate with flow–pressure perturbations in the system.

Skriba, Gockley, and Battaglia have reported in their paper that the new and automated flameless atomic absorption technique is usable as an on-line instrument for the determination of calcium, magnesium, and aluminum in the 0 to 10-ppb range in an operating nuclear power plant.

Fisher has traced the progress that has been made in improving the quality of high-purity water over the past 40 years but admits that the goal of attaining zero impurities has not been attained. She has reported that present purity requirements, particularly those required for specific industries, have exceeded the monitoring ability of the electrical conductivity method, which means that this measurement must be augmented by the inclusion of measurements of specific impurities.

Light and Sawyer have reported that the maximum resistivity of pure water occurs at a pH of 7.039, not 6.998, which corresponds to approximately 0.8 μg/litre of sodium hydroxide. They consider the measurement of resistivity of very pure water to be the simplest and most reliable method of determining its overall purity. They have also pointed out that such measurements should be either carefully temperature compensated or made at the reference temperature.

Lane, Sollo, and Neff have reported on an in-line electric conductivity method for monitoring anions in power plant system waters. This method eliminates interference by amines by incorporating a hydrogen exchanger in the instrument flow and eliminates the effects of temperature variations and

carbon dioxide by measuring conductivity at constant atmospheric boiling water temperature by means of an electric heater. Data show that 1 to 5 μg/litre of $Cl^- + SO_4^=$ can be determined by this technique. More accurate cation conductivity results can be obtained at atmospheric boiling temperature than at 25°C because possible trace amounts [0.01 to 0.05 mg/litre of carbon dioxide (CO_2)] present have a minimal conductivity at this higher temperature. It was also demonstrated that ammonia (NH_3) and CO_2 in a two-component system can be determined from a computer table when pH, conductivity, and temperature values are provided.

Elmiger, Mravich, and Stauffer have reported on a new continuous sample evaporator which has been developed for concentrating the contaminant present in plant systems to levels at which determinations can be made by modern analytical techniques. Chemical species recovery within ±20 percent of the absolute amount added was reported. Further research to investigate the methods of concentration, the effect of sample container materials, and so on are required.

Washinger and Kark have described a polarographic technique for determining chlorine and oxidants at trace levels. It is a method based on the same chemistry as the standard titrimetric methods and the results agree well with those of the amperometric technique. The polarographic technique has the advantage over the amperometric method of being accurate at chlorine equivalents ranging from 100 μg/litre down to 5 μg/litre, at which level the amperometric technique is suspected of failing. This method is reported also to be useful in seawater systems and in determining other types of oxidants.

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