

STATE OF ILLINOIS
WILLIAM G. STRATTON, *Governor*



Hydrogen Exchange Resin for Steam Purity Analysis

by

R. W. Lane, T. E. Larson and J. W. Pankey

Issued by

Department of Registration and Education

VERA M. BINKS, *Director*
State Water Survey Division

A. M. BUSWELL, *Chief*
Urbana, Illinois

Hydrogen Exchange Resin for Steam Purity Testing

R. W. LANE, T. E. LARSON, AND J. W. PANKEY

Illinois State Water Survey, Urbana, Ill.

In the conductivity measurement of condensed steam for purity, inaccuracies result from the presence of carbon dioxide, ammonia, and/or volatile amines. Measurement of conductivity at atmospheric boiling point eliminates major interference by carbon dioxide but only minor interference by ammonia and/or amines. If pretreated condensate is passed through a hydrogen exchange bed, ammonia, volatile amines, and other cations are replaced by hydrogen ion; subsequent reboiling eliminates the free carbon dioxide. The remaining anions are in the form of acids and are readily apparent by their conductance. This method provides a rapid, accurate test for steam purity to indicate deficiencies of feed water treatment, of boiler design, and of plant operation, and limits of safe feed water and boiler solids control. It also detects condenser leakage if ammonia or volatile amines are present in steam condensate.

STEAM produced by the modern steam power plant must be of high purity in order to prevent damage to superheaters, turbines, and other power equipment. High maintenance costs can be expected when impure steam resulting from carry-over of boiler water solids is produced. Also, impure steam when employed in processing may contribute to the contamination of manufactured goods.

By way of definition, steam quality (a measure of B.t.u. content) refers to moisture content as H₂O, whereas steam purity refers to ingredients other than H₂O which might be present. Whether the particular ingredients are desirable, unimportant, or harmful need have no place in a basic definition. Likewise, causative factors need no place in the definition.

From an academic standpoint, any divergence of conductivity from 0.054 micromho per cm. at 25° C. should be an indication of the presence of impurities, whether they be gaseous or mineral. The object of all steam purity testing is to observe or record deviations from a uniform recording of conductivity. The limits of impurities of various types have been neither completely identified nor quantitatively defined for various operating conditions. Pure steam or condensate or water meeting the above definition is not necessary and probably not desirable.

Steam impurities may be of the volatile class which includes silica, carbon dioxide, sulfur dioxide, ammonium, the volatile and filming amines, and oil, or of the nonvolatile class which includes mineral ingredients obtained from mist, spray, prime, or other causes.

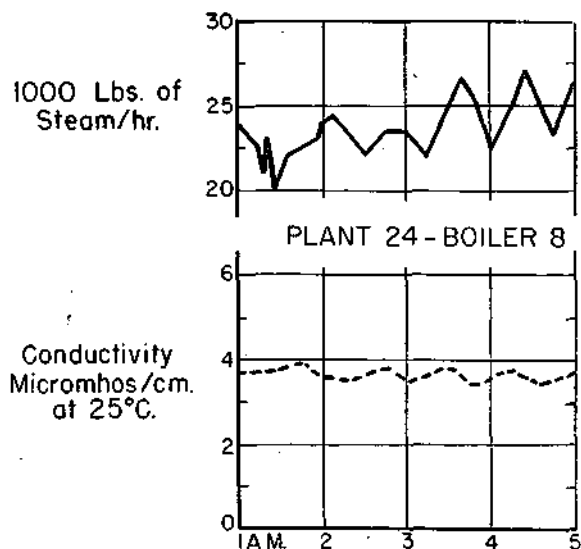


Figure 1. Conductivity Measurements Showing Effect of Varying Percentages of Make-up Water, on Ammonia Content of Steam

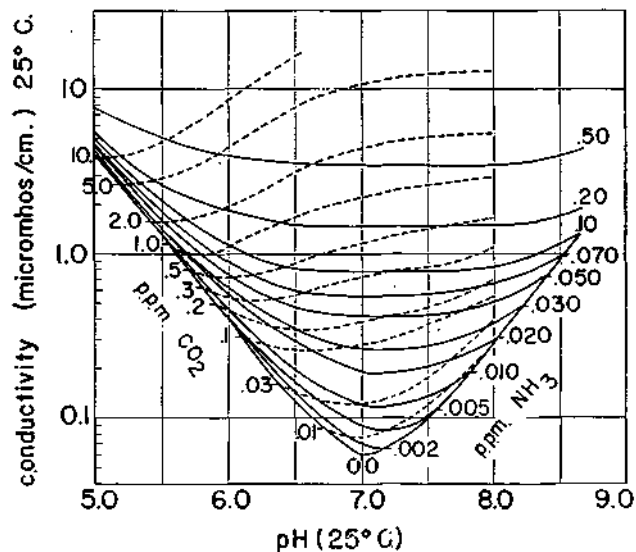


Figure 2. Equilibrium Constants for Carbon Dioxide, Ammonia, pH, and Conductivity Relationships

The presence of volatile impurities in steam and condensate is subject to the laws of chemical equilibria and is dependent primarily on rating, pressure, and boiler water concentrations. The design of boiler drum internals may also influence the resultant concentration of volatile compounds, particularly sulfur dioxide and silica, in steam to a greater or lesser degree. Also, steady state conditions in the boiler are proportionally upset by increasingly rapid changes in load. Sampling and testing procedures for the volatile components are usually of more specific interest at the particular points of potential harm.

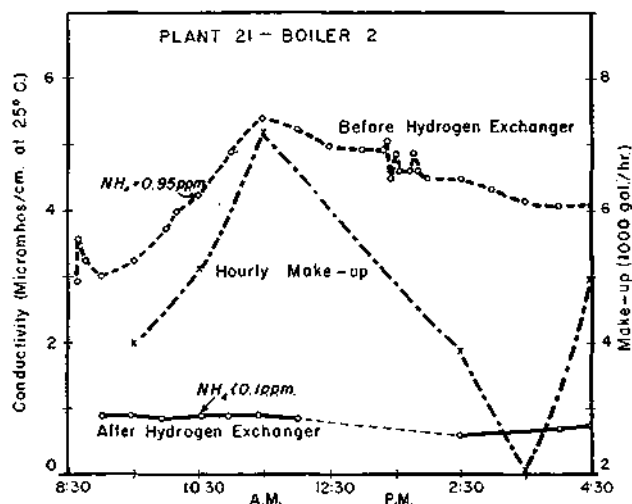


Figure 3. Conductivity Measurements at Plant 21

The presence of nonvolatile impurities is not governed by chemical equilibria and may or may not be expected to be quantitatively dependent on rating, pressure, or boiler water concentration but to a large extent is dependent on design and water treatment. Deviation from a uniform conductivity may be considered as abnormal. Appropriate sampling and testing procedures for the abnormal presence of nonvolatile impurities (carry-over) are of primary importance.

Steam purity measurements have, therefore, been found to be important in the design of boiler internal baffling, of steam purifiers, and of feed water treatment, as well as in the control of plant operating variables, such as water level, boiler load, firing practices, and feed water treatment.

During the past 30 years, measurements of steam purity have been made principally by calorimetric, gravimetric, and conductometric methods (2, 4). The conductometric method, however, is the most accepted method because it is the simplest, most sensitive, and speediest. Its main disadvantage has been the interference provided by gases, such as carbon dioxide, ammonia, and more recently, amines, which have significant conductivities when condensed.

This interference problem became acute in studies on steam purity at Illinois State Institutions supplementing the Feed Water Treatment Service provided by the Illinois State Water Survey. In the institution type plant, a variable percentage of make-up water is employed from hour to hour. This produces a widely varying ammonia content in the steam. When the ammonia recycles through the plant system, the interpretation of the recorded conductivity is further complicated. Such conductivity results at two plants are shown in Figure 1 and Figure 3.

The early tests used a modified Straub degasifier or constant temperature device to provide a simple control of the constant temperature required for conductivity measurement.

The steam was injected in the degasifier and condensed in a

vented chamber containing a cooling water coil. Sufficient cooling was provided to maintain a constant temperature of about 210° F. at atmospheric pressure. A single point strip chart recorder of 0-40 and 0-1200 micromho ranges was employed to measure the conductivity of the condensed steam. This instrument, when employing an electrode with a cell constant of 0.1, recorded the conductivity in micromhos per centimeter, corrected to a temperature of 25° C. The advantages of this measurement of the conductivity at 210° F. were the accuracy and the simplicity of the temperature control of the condensate near the atmospheric boiling point of water.

This device, however, was found to be only partially efficient in the removal of ammonia.

Applying corrections for the ammonia and/or carbon dioxide contents was found to be tedious, and inexact, because of the varying gas contents and the frequent analyses required. A new graph (Figure 2) employing the latest equilibrium constants (6) was prepared for the carbon dioxide, ammonia, pH, and conductivity relationships, but this also did not serve the purpose of simple interpretation of results.

The specific application of this chart is limited by the low confidence in the results of direct Nesslerization for ammonia (± 0.1 p.p.m.) and by the lack of information on the temperature coefficient of the individual ionic conductances as well as the equilibrium constants, unless the tests are made at 25° C. Both of these limitations may be overcome in time.

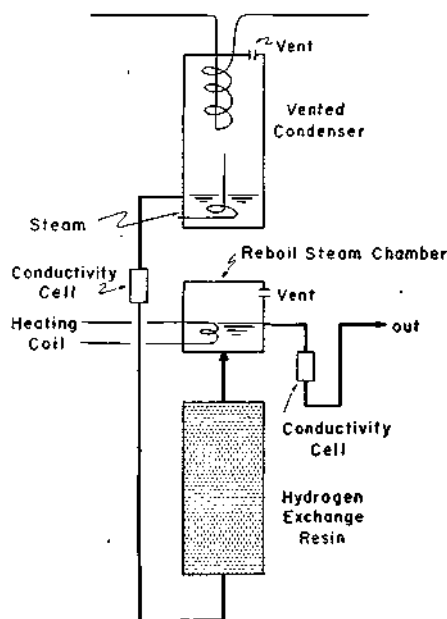


Figure 4. Steam Purity Analyzer Equipment

The futile attempts to apply corrections for ammonia and carbon dioxide interference led to a decision to remove the gas prior to the measurement of conductivity by incorporation of a hydrogen exchanger in the system, following the boiling point condensation. Subsequent reboiling was provided to remove remaining carbon dioxide at the more favorable low pH conditions resulting from the hydrogen exchange.

Although it was anticipated that carry-over conductivity due to hydroxide and carbonate would be lost by the ion exchange and reboiling processes, it was also recognized that the increased conductivity of the resultant hydrochloric and sulfuric acid would more than compensate for this loss and actually increase the sensitivity of the measurement. Calculations revealed that the

conductivity of the acids was about 3.3 times the conductivity of the corresponding sodium salts, and therefore more than 50% of the boiler solids would have to be of hydroxide and carbonate salts before any decrease in conductivity would result from the ion exchange.

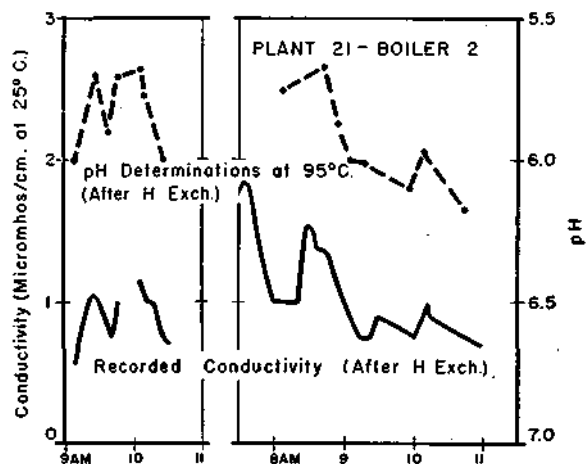


Figure 5. Continuous pH Measurements Following Hydrogen Exchange

The procedure proved to be successful (Figure 3). Since the gas contaminants were reduced to a minimum, any increase in conductivity was now attributed with certainty to be mineral carryover (5).

TEST METHODS

Saturated steam was sampled from institutional power plant boilers producing steam at the rate of 20,000 to 50,000 pounds per hour at 125 to 250 pounds per square inch pressure. Steam sampling nozzles were installed according to the ASME specifications (1). One-quarter inch copper and stainless steel tubing carried the steam from the nozzle to the stainless steel or brass degasifiers.

Following condensation in the constant temperature device, the condensate was passed through a 4-inch diameter bed of polystyrene resin (0.04 cu. ft.) in the hydrogen cycle, then through a reboil chamber, where the temperature was brought back to

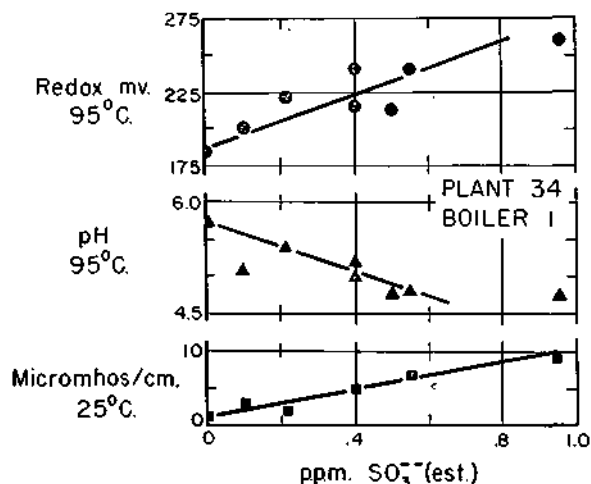


Figure 6. Conductivity, pH, and Redox Potential Measurements Following Application of Sodium Sulfite to Effluent from Vented Condenser

210° F. as in the original chamber. Sampling locations were provided for measuring the conductivity previous to and following the hydrogen exchange in order to determine the effectiveness of this process in removal of the interfering substances. Figure 4 shows the complete steam purity testing equipment.

In these tests, chemicals were fed with the boiler feed water direct to the boiler by means of a chemical feed pump or a pot feeder connected to the boiler feed line.

Considerable differences of opinion (1, 3, 8) have been reported as to proper sampling rates, so the authors chose a more or less average rate of 40 to 60 pounds per hour, in order to avoid liquid films and corrosive effects associated with the lower sampling rates and to avoid the excessive loss of condensate associated with higher sampling rates.

TEST RESULTS

As anticipated, continuous pH measurement following hydrogen exchange also indicated steam purity (Figure 5).

The application of sodium sulfite to the effluent from the boiling point condenser provided parallel indications of its presence when measurements were made of conductivity, pH, and redox potential (Figure 6).

At plant 21, cyclohexylamine was applied hourly with other

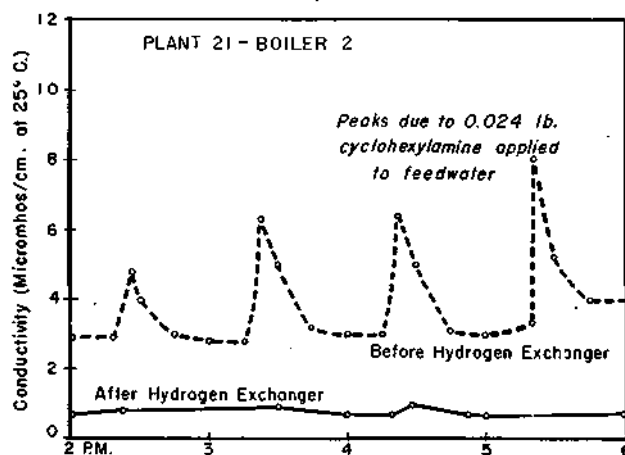


Figure 7. Conductivity Measurements of Cyclohexylamine Treated Water before and after Hydrogen Exchange Treatment

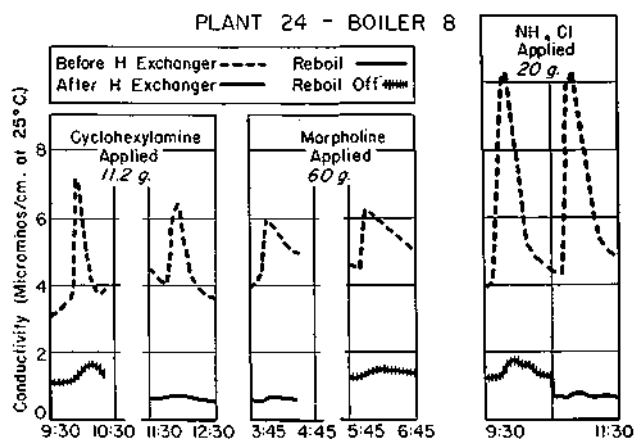


Figure 8. Hydrogen Exchange Treatment Plus Reboil Eliminated Effects of Cyclohexylamine, Morpholine, and Ammonium Chloride Used for Condensate pH Control to Prevent Corrosion

boiler feed water treatment by means of an electrically operated pump. Prior to the application of the hydrogen exchange process, the interpretation of the conductivity data would have indicated a serious boiler water carry-over problem. However, the ion exchange process eliminated this interference and indicated that good steam purity was being provided (Figure 7).

At plant 24, application of cyclohexylamine, morpholine, and ammonium chloride (9), chemicals normally employed for condensate pH control for corrosion prevention, revealed that the hydrogen exchange process plus reboil eliminated the interference provided by these chemicals (Figure 8).

Preliminary tests on the effect of octadecylamine (7), a filming amine employed to prevent condensate corrosion, indicate that this amine, apparently due to its low solubility and ionization, does not appreciably influence the conductivity results.

When these data were discussed with F. G. Straub, at the University of Illinois, he designed a small unit without temperature control for testing condensate to determine condenser leak-

age in power plants employing ammonia or amines for condensate pH control (Figure 9). It was estimated that immediately after installation the results detected a 0.01% condenser leakage (Lake Michigan water).

CONCLUSIONS

By combining the procedure of temperature control at the atmospheric boiling point and the hydrogen exchange process with reboiling, an easy foolproof method of testing steam purity has been developed. This method minimizes interference from carbon dioxide, ammonia, cyclohexylamine, and morpholine; provides a simple temperature control; and detects boiler water carry-over by continuous conductivity, pH, or redox measurement.

LITERATURE CITED

- (1) Am. Soc. Mech. Engrs., 29 W. 39th St., New York, Power Test Code, "Determination of Quality of Steam, Part II," 1940.
- (2) Am. Soc. Mech. Engrs., 29 W. 39th St., New York, Steam Contamination Subcommittee of the Joint Research Committee on Boiler Feedwater Studies, "Bibliography on Steam Contamination."
- (3) Am. Soc. Testing Materials, Committee D 1066-49T, "Tentative Method of Sampling Steam," 1949.
- (4) *Am. Soc. Testing Materials, Proc.*, 41, 1261-1340 (1941).
- (5) Lane, R. W., Larson, T. E., and Pankey, J. W., *Proc. 14th Ann. Water Conf., Engrs. Soc. West. Penn.*, 119-39 (1953).
- (6) Latimer, W. M., "Oxidation Potentials," Prentice Hall, New York, 1952.
- (7) Maguire, J. J., *IND. ENG. CHEM.*, 46, 994 (1954).
- (8) Place, P. B., *Combustion*, 23, 49-53 (April 1951).
- (9) *Proc. 14th Ann. Water Conf., Engrs. Soc. West. Penn.*, "Panel Discussion on Corrosion and Deposits in Condensate and Feedwater Systems" (1953).

RECEIVED for review March 29, 1954.

ACCEPTED September 23, 1954

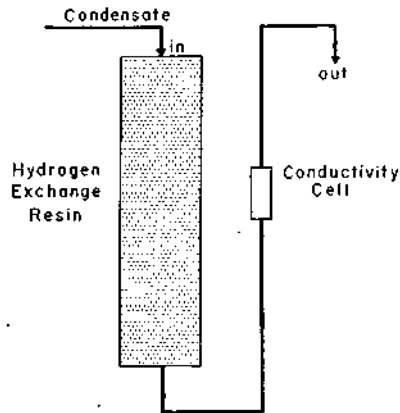


Figure 9. Condensate Analyzer Equipment