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Experimental Investigations of the Effect the Electrical Conductivity of Medium Has on the Performance of pH Meters

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Abstract—Results from tests of pH meters carried out in ammonia media having low electric conductivity (less than 5.0 μS/cm) are presented. The check media for the tests were prepared in a special manner the use of which makes it possible to reproduce the pH value of solution with an error not exceeding ~0.04pH in the range of electrical conductivities above 0.1 μS/cm. The instrument measurement error was determined at different electrical conductivities of medium. Different electrodes were tested, the majority of which were domestically produced ones intended for general industrial applications. Some results were also obtained for one dedicated electrode from a foreign manufacturer. The test results show that the instrument gives a biased pH value for such media. The bias has a random value, which nonetheless is stable in the majority of cases, depends on the electrical conductivity of medium being monitored, and may be quite essential for small electrical conductivities (0.5pH or more). A conclusion is drawn about the need to calibrate the instruments with respect to standard media having electrical conductivity close to that of the medium being monitored. Analytic relations characterizing the check media used fort tests (check solutions) are presented.

Keywords: weakly conducting media, pH measurement error, biased pH estimate, checking, calibration of pH meters, weakly conducting standard solutions, calculating the pH value of standard solution

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The pH value of process media used in power-generating facilities is one of the most important indicators characterizing the corrosion activity of these media. This indicator is standardized and is subject to mandatory periodic (manual) or continuous (automatic) checking [1–3]. Based on the results of measurements, the water medium is subjected to correction by adding the appropriate reagents in order to bring the pH value to the required level.

The accuracy with which the pH value of medium has to be maintained determines the requirements imposed on the maximum permissible error of measurement instruments. For some media, the range within which the pH value may deviate from its preset level must not exceed ±0.1pH [1]. The pH value can be maintained at a preset level by using an instrument the measurement error of which does not exceed ±0.05pH. If the instrument has a larger measurement error, it becomes difficult to solve such a task.

Instrument-assisted measurement of pH is as a rule performed by the potentiometric method with the use of the classic electrode pair consisting of a glass pH electrode and an electrode for comparison with a salt bridge. The typical measurement errors determined on standard buffer solutions are in the range (0.01–0.03)pH. As a rule, the relevant technical documents specify the instrument measurement error at a level of ±0.05pH. Formally, such instruments are well in conformity with the tasks imposed on the metering of pH values in thermal power engineering.

At the same time, it is commonly known that the electrical conductivity of water media used at thermal power facilities lies predominantly in the range from 0.055 μS/cm (which corresponds to the electrical conductivity of theoretically pure water at 25°C) to approximately 1.0 μS/cm. The electrical conductivity of media containing an alkalizing reagent is in the range 3.0–5.0 μS/cm. Such media differ drastically from standard buffer solutions, the conductivity of which exceeds 1000 μS/cm. It can be expected that the measurement errors in weakly conducting media may differ very considerably from those in buffer solutions.

Attempts to estimate the performance of pH-metering instruments on weakly conducting media involve well-known difficulties stemming from the lack of required buffer solutions with similar conductivity.

The error with which pH values are measured in weakly conducting media can be estimated by constructing an appropriate model of medium being monitored and theoretically calculating the pH value from the measured values of the other parameters of this medium (electrical conductivity, temperature, and concentration of particular reagents). After that, the error of instrument-assisted measurement is deter-