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High-precision determination of potassium hydrophthalate content by a method of coulometric titration in a horizontal type of electrochemical cell

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Abstract The main aim of the work was high-precision determination of potassium hydrophthalate content by coulometric system with horizontal type cell. The coulometric system was developed for functioning of the State primary standards of pH GET 54-2011 and pX GET 171-2011 ions activities in liquid media. The coulometric system is necessary to ensure the procedures for monitoring the purity of chemical reagents used in the production of high-cleaning reference substances, which used as working standards. High-clean substances are used to prepare mixtures and solutions for metrology area, particularly they are used in the State primary standards key comparisons, as well as, to direct transfer of units of quantify characteristics of chemical substances used in the calibration or verification procedures of measuring instruments, in certification of standards, in control of precision of measurement methods.

1. Introduction

Coulometry is a reliable, simple, highly sensitive method that allows for analysis with high accuracy (the error in direct coulometry is \( \sim 0.05 \div 0.1\% \), and in coulometric titration \( \sim 0.1 \div 0.3\% \)). The advantage of the coulometric method is the determination of small impurity contents \( (10^4 \div 10^5\% \text{ by weight}) \). Also this method has the expressness, which makes it possible to automate the monitoring process remotely. Coulometric titration is advisable to use for the substance being determined, since the relative standard deviation is usually 0.001-0.01 \([1]\).

High-purity substances are widely used in metrological works as vectors of information on the chemical composition in the initial and final interval of the scales of the mass (molar, volumetric) fraction of the component, as well as the pH scale. When transferring high-purity substances to a solution, they carry information on the pH value in the range from 0 to 14. Applied to the activity indices of the pX-ions, the mass (molar) concentration of the component in the middle and the beginning of the measurement range, and thus, cover all possible range of shares from 0 to 100\%. Usually, high-purity substances serve for the preparation of mixtures and solutions for metrological
purposes, in particular, when working with the State primary standards are used for perform comparisons in the field of basic measurement capabilities, and are also used directly to transfer units of quantities characterizing the chemical composition in calibration and calibration work measuring instruments, attestation of standards, control of the accuracy of measurement procedures.

At FSUE VNIIFTRI, a standard pH scale was created to reproduce, store and transmit the value of the hydrogen index, as the state primary one under the registration number GET 54-98. This primary standard was designed to reproduce, store and transmit a pH scale in the range of 3.547 to 10.317. In 2011, the standard was improved and received the name of the State Primary Standard for the pH of the activity of hydrogen ions in water solutions of GET 54-2011. The improvement was carried out by introducing into its composition two new buffer solutions, which allowed to expand the limits of pH reproduction in the range 1 to 12. For measure pH in the new standard, the method of measurement based on the Harned electrochemical cell was used in accordance with the recommendations of IUPAC 2002 [2].

During the exploitation of the GET 54-2011, in some cases, a perceptible change in pH values was noted at the same masses of the sample weights (e.g., potassium hydro phthalate) used to prepare the standard buffer solution. It should be noted that this displacement was observed only when the potassium hydro phthalate batch was changed, from which the standard substances were made. In view of this, it was assumed that this change occurs due to the influence of impurities in the potassium hydro phthalate. Therefore, there was an acute need to determine the main substance (potassium hydro phthalate), for evaluation the content of impurities in it, and to control the degree of purification, after carrying out the process of recrystallization.

2. Technique of experiments

2.1. Method for preparing solutions
To ensure the operation of the coulometric installation, it is necessary to prepare a solution of potassium nitrate (KNO₃) at a concentration of 2 M, which serves to prepare the agar-agar plug (electrochemical bridge). To do this, we weighed a sample of mass m = 202.2 g of KNO₃ dry salt and placed in a 1-liter volumetric flask. Then, we added deionized water to the notch and mixed until the sample was completely dissolved. To prepare a solution of the background electrolyte, weighed a sample weighing m = 149 g. Potassium chloride salt and dissolved it in a 2-liter volumetric flask, adding deionized water. Potassium chloride dissolves well in water.

For the preparation of sample necessary for analysis on a coulometric installation, we weighed a sample of mass m = 5 g of potassium hydro phthalate and dissolved it in 50 ml of water. Complete dissolution of potassium hydro phthalate occurs at room temperature for ~ 15 minutes. For the analysis, two samples were prepared, one from domestic potassium hydro phthalate, and the other from imported potassium hydro phthalate, which was sent for international key comparisons conducted by the inorganic analysis group at the International Bureau of Weights and Measures as part of confirming the measurement capabilities of the state primary standards of the inorganic analysis area.

All salts used for the preparation of solutions were pre-thermally treated to remove moisture at a temperature of 110 °C for 2 hours.

It should be noted that the water used for the preparation of solutions had a degree of purity of 1 according to GOST R 52501 with a specific electrical conductivity of not more than 0.01 mS / m at a temperature of 25 °C.

2.2. Method of preparation of electrochemical bridge
For preparation an electrochemical bridge, we weighed a sample weighing m = 5 g of dry agar, which was then dissolved in 100 ml of 2 M potassium nitrate. The KNO₃ solution was preheated in a heat-resistant beaker to about 70 °C. Agar-agar was added in small portions to the solution by constantly mixing to ensure homogeneity of the medium and uniform agar-agar congealing.
After the mixture became thick and uniform (~ 7 ÷ 10 minutes), the glass was cooled. This is necessary for the conversion of agar-agar into a gelatinous state and the formation of a jelly-like bung. Cooling was carried out under running tap cold water for 10 minutes, and then the contents of the glass were poured into the chamber of the coulometric cell, so as to completely separate the working spaces of the coulometric cell. Then, for 35 minutes, the cell was left at room temperature until the agar bung solidified completely.

2.3. Technique of work with the coulometric installation

To determine the main component in the solution of potassium hydrophthalate, a coulometric installation was created, shown in figure 1.

![Scheme of coulometric installation](image)

**Figure 1. Scheme of coulometric installation.**

The process of performing measurements of the mass fraction of the main substance in the analyzed sample by coulometric method consists of three stages of titration: preliminary, basic and final. Preliminary and final titration was carried out at low generator currents (1 ÷ 5 mA), in batches flowing current through the cell. After each portion of the transmitted quantity of electricity, we recorded the change in the indicator signal (pH, pX or indicator current, which depends on the method of indicating KTT) and from these data we plotted the titration curve in pH coordinates (pX or Iind) = f (t). The main titration is carried out at a large generator current (50-100 mA) during the time calculated by Faraday’s law, taking into account that approximately 0.1 mg of the sample remains unreacted (the excess titrant remaining after the preliminary titration was taken into account). At the end of the experiment, we calculated the total amount of electricity spent on titrating the sample of the substance at all three stages of the experiment.

Before carrying out the experiments, approximately 200 ml of a background solution of electrolyte were poured into the chambers of the electrochemical cell. To ensure mixing and uniformity in the in the chamber with sample, a magnetic stirrer was provided.

Before the experiment, to remove dissolved carbon dioxide, the electrolyte solution was scavenged with an inert gas (Argon) for 40-60 minutes. Carbon dioxide is very soluble in water, and a weak, unstable carbonic acid is formed which can dissociate into ions and lead to an increase in the ion concentration:

\[
\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3
\]
In general, the dissociation reaction proceeds only through the first stage, since carbonic acid is a weak acid. Scavenging with argon allows partial displacement of carbon dioxide. After this, a preliminary titration procedure is carried out, during which excess hydrogen ions, which are in solution due to acidification and not removed carbon dioxide, are titrated. From the ingress of carbon dioxide with air during titration, the argon layer protects the electrolyte, where argon accumulates above the electrolyte during scavenging, since argon is heavier than air.

The main element of the coulometric installation is the potentiostat P-30J. Potentiostat allows you to work on two, three or four-electrode circuits connecting to an electrochemical cell, both in potentiostatic and in galvanostatic modes. The control programs included in the delivery package allow fully controlling the device and operating with the registered data from a personal computer.

To work with the potentiostat, we ran the control program that was used to build the "potential-time" graph and entered the initial pre-calculated values of the titration time, the amperage and the number of titration cycles. Then the electrolyte solution was "burnt" without a sample for remove impurities and unwanted ions in solution. For this purpose, the program was given additional time (200 s.), which included the "burning" of the electrolyte.

With the stabilization of the "potential-pH" graph, we supplied current and ran the program for plotting the "potential-time" graph. The first 100 seconds of the experiment carried out a "burn" of the solution without a sample. After 100 seconds, a sample was introduced into the electrochemical cell.

The measurements were carried out according to the calculated time and quantity of charge, which is necessary for the complete passage of the electrochemical reaction taking into account the margin of 10%.

The indicator of the completion of the electrochemical reaction was the registration of the end point of titration with the help of a pH measuring electrode.

After the experiment was completed, the data obtained was mathematically processed.

3. Results of experiment behavior

"Trial" experiments were carried out to evaluate the content of interfering impurities in the background electrolyte. In these experiments, a sample of potassium hydrophthalate was not introduced into the coulometric cell. The total titration time in the experiments was 2000 seconds with a voltage of the appropriate current strength of 3mA, 50mA, 10mA. The results of the experiment are shown in figure 2.

![Figure 2](image.png)

**Figure 2.** Type of titration curve of the "Trial" experiment in coordinates "pH - time" with a current strength of 3 mA, 50 mA, 10 mA.
From the results obtained, one can see the absence of extraneous peaks in the diagrams in all areas of the titration. Thus, the purity of the electrolyte used was confirmed.

The next stage of the work was aimed at determining the content of the main component of potassium hydrophthalate in imported and domestic samples. Figure 3 shows the result of the experiment in the form of a titration curve for an imported sample.

**Figure 3.** Determination of the end point of titration of the imported sample of potassium hydrophthalate.

The titration end point obtained in the experiment was 112.19 seconds, which corresponds to a mass fraction of the main component of 99.9712%.

To determine the end point of the titration, experimental data corresponding to a minimum of voltage values were twice differentiated. The criterion for achieving a finite titration time was the value of the modulus of the second differential tending to zero. In a similar way, experiments were carried out for the domestic sample. The results of the experiments are summarized in Table 1.

**Table 1. Summary of the determination of the main amount of the substance in potassium hydrophthalate.**

| Name of the value                                      | Import sample | Russian sample | Comparison results CCQM-K34 |
|-------------------------------------------------------|---------------|----------------|-----------------------------|
| Content of the main component, mol / kg               | 4.89527       | 4.89635        | 4.89545                     |
| Uncertainty of the determination of the main component, mol /kg | 0.000211      | 0.00020        | 0.000208                    |
| Mass fraction of the main substance, %                | 99.9712       | 99.9933        | 99.9745                     |
| Inaccuracy in the determination of the basic substance, % | ± 0.0017      | ± 0.0017       | ± 0.0017                    |
| Mass fraction of impurities, %                        | 0.0288        | 0.0067         | 0.0255                      |
As can be seen from the obtained results, the Russian sample is a cleaner chemical substance in comparison with imported analogs. The table shows the results of international key comparisons carried out within the measurement capabilities of the world’s leading metrology institutes. When comparing the obtained data with the results of comparisons, close values of foreign samples become apparent. The greater value of the mass fraction of the domestic sample is due to the preliminary purification of potassium phthalate by triple recrystallization from a hot solution.

4. Conclusion
Thus, a coulometric installation based on a horizontal electrochemical cell was created to determine the main part of a substance by coulometric titration. The bulk of the potassium phthalate component was determined for domestic and imported samples. When comparing the results obtained, it turned out that the value of the main part of the component of the imported sample coincides, within the experimental error, with the results of international key comparisons, which indicates the correctness of the choice of the method and approach for creating the experimental installation.

5. References
[1] Kabanova OL 1969 electrochemical methods of analysis of inorganic substances in aqueous solutions (Moscow: Nauka, p 256)
[2] Agasyan P K1984 coulometric analysis method (Moscow: Chemistry, from 168)