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## Influence of buffer quality on pH measurement uncertainty: prediction and experimental evaluation

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**Abstract** Dependence of the uncertainty of a pH measurement result on the quality of buffers (i.e. the uncertainty of their certified pH values) at different levels of instrumental uncertainty (pH-meter, etc.) was simulated using the Monte Carlo method and regression analysis. The contribution of the instrumental standard uncertainty (in the studied range from 0.1 to 1 mV) to the uncertainty of the pH measurement result is negligible, if the standard uncertainties of the pH buffers exceed 0.04 pH (e. g. for in-house buffers). It is shown how the choice of pH-meter and buffers should be correlated in order to meet the required uncertainty of a pH measurement result in a sample under analysis. The results of

the simulation were compared with experimental data obtained from calibrations of a pH/ion-meter with a hydrogen working electrode (Radiometer PHM-240) and with a glass electrode (Metrohm 744). Buffers of different quality (National Institute for Standards and Technology standard reference materials, certified Radiometer buffers and Merck CertiPUR buffers) were used for the calibrations. The uncertainties of the experimental results are close to the predicted ones obtained by the simulation.

**Keywords** Measurement uncertainty · pH · Monte Carlo method · Calibration · Buffers

### Introduction

A number of buffers with different standard uncertainties of certified pH values are available on the market (from 0.0025 for National Institute for Standards and Technology standard reference materials – NIST SRMs – to 0.025 for BDH concentrated buffer solutions, for example), others can be prepared as “in-house” reference materials. Instrumental measurement standard uncertainties are also different (from 0.1 mV for a Radiometer PHM-240 pH/ion meter to 1 mV for a Metrohm 744, for example). It is important to consider the uncertainties for buffers and instruments as quality parameters that are used to ensure the required uncertainty of the pH measurement in samples under analysis.

The most important fields where accurate pH measurement is required are environmental protection, pub-

lic health care and biotechnology [1]. Correct calibration of pH-meters referring to precise pH standard solutions (buffers) is very important in these fields [2]. According to ref. [3], the standard deviation of pH value for measurements in clear laboratory aqueous solutions shall not exceed 0.01 pH while using a multi-point calibration method with precise buffers.

In the present work prediction of the influence of buffer quality on pH measurement uncertainty is performed using Monte Carlo simulations and regression analysis. The results of the simulations are compared with experimental data obtained by calibration of pH measurement systems.

## Predictions

### Simulation

The pH simulation was based on calculation of the "true" pH value  $pH_{tr}$  for a buffer. This value deviated randomly from the buffer certified value  $pH_{cer}$  within the range of its expanded uncertainty  $U_{pH}$  (0.005–0.15 pH). The value of random deviation  $\zeta$  had normal distribution with mathematical expectation of zero and standard deviation  $u_{pH}$  equal to  $U_{pH}/2$ . Thus, the Monte Carlo simulation [4] in our case can be performed using the following equation:

$$pH_{tr} = pH_{cer} + \zeta \\ = pH_{cer} + \sqrt{-2u_{pH}^2 \log(1-\rho)} \sin(2\rho'\pi), \quad (1)$$

where  $\rho$  and  $\rho'$  are random numbers with uniform distribution from 0 to 1. Three replicate  $pH_{tr}$  values were calculated for each  $pH_{cer}$ .

The electromotive force  $E$  is calculated by the Nernst equation for the "true" pH value:

$$E = 0.208 + 0.05916pH_{tr}, \quad V, \quad (2)$$

where 0.208 is the potential of a Ag/AgCl reference electrode in 3 M KCl, 0.05916 is the Nernst coefficient at 25° C. The  $E$  value was changed randomly to  $E'$  within the range of instrumental expanded uncertainty  $U_E$  using the Monte Carlo algorithm:

$$E' = E + \sqrt{-2u_E^2 \log(1-\rho)} \sin(2\rho'\pi), \quad V, \quad (3)$$

where  $u_E = U_E/2$  is the standard instrumental uncertainty. Three calculated  $E'$  values (for the three replicate  $pH_{tr}$  values) at the corresponding  $pH_{cer}$  were averaged to  $E_{av}$ . The simulation was performed 1000 times for 6 buffers with  $pH_{cer} = 3.5, 4, 7, 7.5, 9$  and 10.

A linear dependence of  $E_{av}^i$  on  $pH_{cer}^i$  of the  $i$ -th buffer, i.e. the calibration curve  $E_{av} = a + b \cdot pH_{cer}$ , was estimated by the ordinary least square method [5] for different instrumental and pH buffers uncertainties ( $a$  and  $b$  are the regression coefficients – the intercept and the slope, correspondingly). The residual standard deviation  $S_{res}$  for the calibration curve was calculated by the following equation:

$$S_{res} = \left\{ \frac{\sum_i (E_{av}^i - \hat{E}_{av}^i)^2}{n-2} \right\}^{1/2}, \quad V, \quad (4)$$

where  $\hat{E}_{av}^i$  is the value of  $E_{av}^i$ , predicted using the calibration curve,  $n=6$  is the number of buffers.

### Bivariate regression analysis

It is important to note that the uncertainties in pH-certified values of buffers used for calibration violate one of the basic postulates of ordinary least square analysis, according to which uncertainty should be associated with the values on the ordinate axis only. The slope of a calibration curve when both axes are subjects to errors can be evaluated by bivariate regression analysis [6, 7] using the following formula [8]:

$$b' = \frac{bS_{pH_{cer}}^2}{S_{pH_{cer}}^2 + u_{pH}^2}, \quad (5)$$

where

$$S_{pH_{cer}}^2 = \sum_{i=1}^n (pH_{cer}^i)^2 - \frac{\left( \sum_{i=1}^n pH_{cer}^i \right)^2}{n}. \quad (6)$$

The bias in results of pH measurements caused by the difference between  $b'$  and  $b$  was calculated by the following equation:

$$\Delta pH = \frac{E_{av} - a}{b} - \frac{E_{av} - a'}{b'}, \quad (7)$$

where  $a'$  is the intercept of the calibration curve calculated by bivariate analysis.

The dependence of  $\Delta pH$  value on the uncertainty  $u_{pH}$  is shown in Fig. 1 for different ranges of pH calibration and different numbers of buffers used for the calibration. As one can see,  $\Delta pH$  increases with a decrease of the calibration range. The same dependency is observed with a decrease of the number of buffers: the robustness of the ordinary square analysis against the violation of the dis-

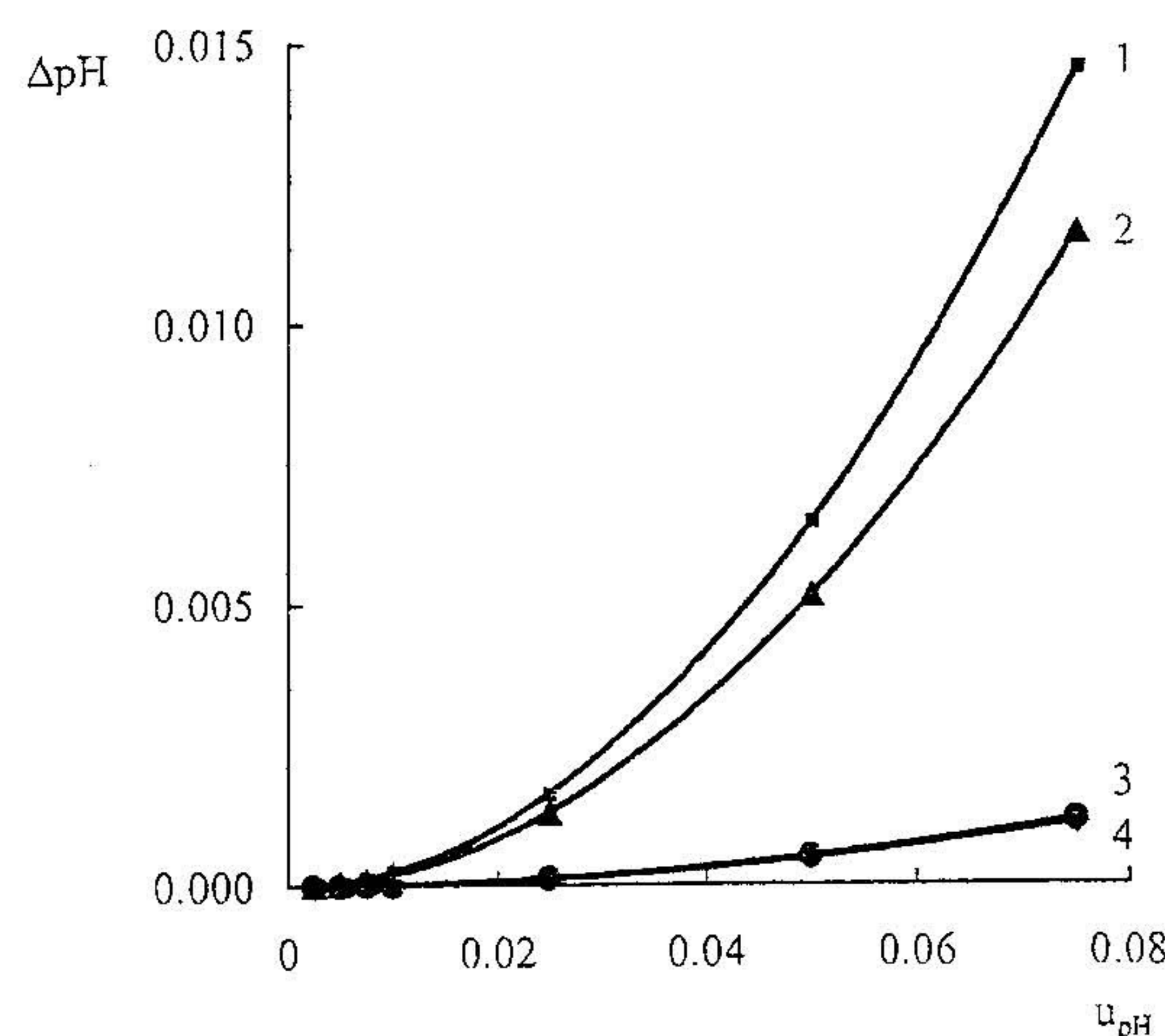


Fig. 1 Dependence of the bias  $\Delta pH$  (caused by the difference between ordinary square analysis and bivariate analysis of calibration data) on uncertainty  $u_{pH}$  of certified pH values in buffers used for the calibration. Lines 1 and 2 correspond to the pH calibration range 6–8 with 4 and 6 buffers for the calibration, respectively; lines 3 and 4 – to the pH range 3.5–10 with 4 and 6 buffers used for the calibration, respectively.

cussed postulate is increasing with the number of calibration data. However,  $\Delta\text{pH}$  does not exceed 0.001 pH under the simulation conditions (6 buffers with pH from 3.5 to 10) and, therefore, is negligible here. It corresponds to the current state of the art for pH measurements [9].

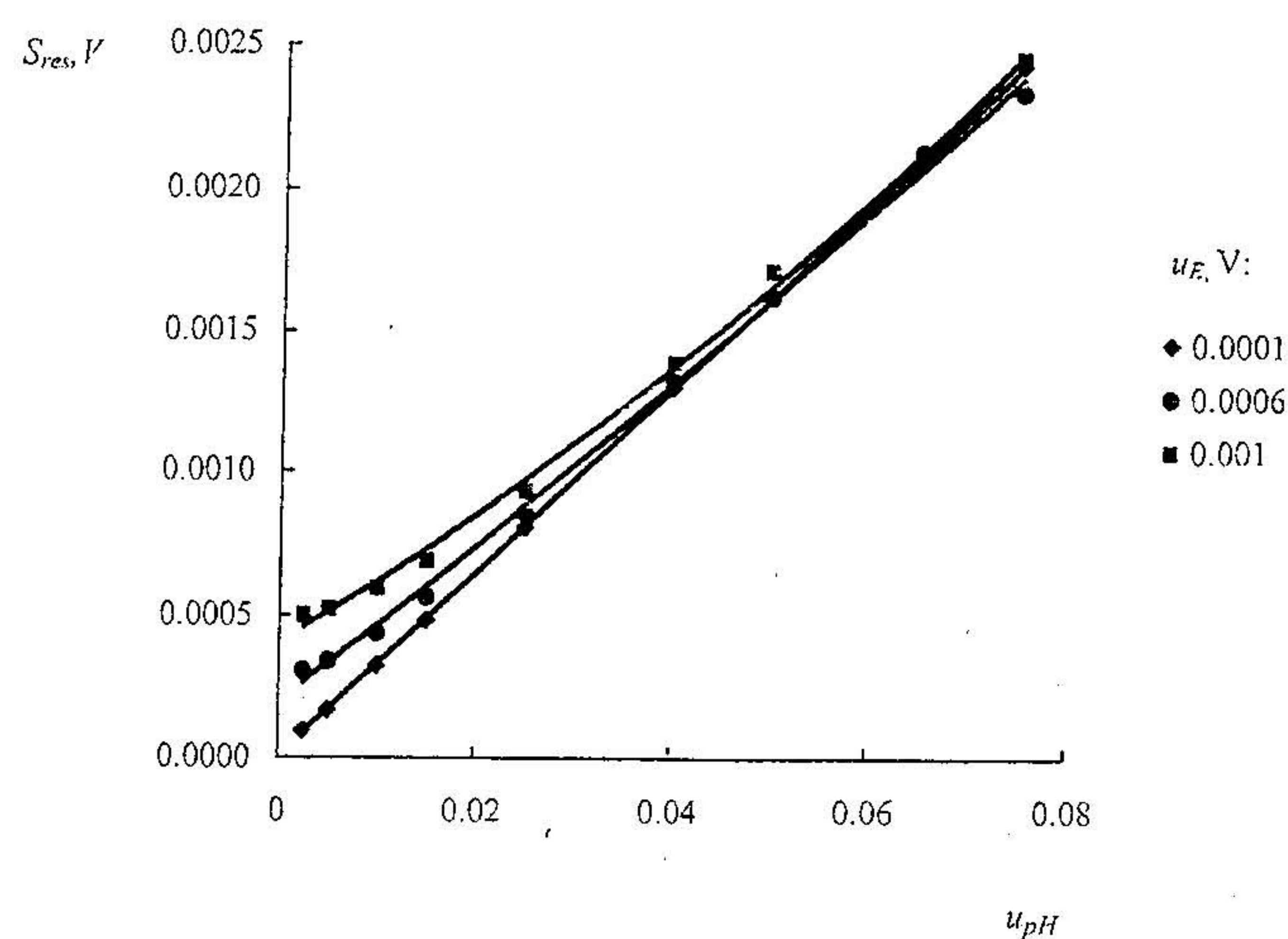
## Models

The dependence  $S_{\text{res}}$  on  $u_{\text{pH}}$  (Fig. 2) is described successfully by quadratic polynomial models found with the use of ordinary regression analysis. The coefficients of these polynomials are presented in Table 1. Obviously, the slopes and intercepts of the calibration curves  $E_{\text{av}}$  vs.  $\text{pH}_{\text{cert}}$  have the same type of dependence on  $u_{\text{pH}}$  [5]. One can see from Fig. 2 that the influence of  $u_{\text{E}}$  on  $S_{\text{res}}$  is negligible, if the uncertainty of pH buffers  $u_{\text{pH}} > 0.04$  pH. In general, the residual standard deviation depends on the instrumental uncertainty less than on the pH uncertainty of buffers in the ranges studied, as shown in Fig. 3.

The standard uncertainty  $u_0$  of a result of pH measurement in a sample under analysis (with  $\text{pH}_0$ ), caused

**Table 1** The polynomial coefficients  $b_0$ ,  $b_1$ ,  $b_2$  and the square of correlation coefficient  $R^2$  of the dependence of residual standard deviation  $S_{\text{res}}$  on pH uncertainty of buffers  $u_{\text{pH}}$ :  $S_{\text{res}} = b_0 + b_1 u_{\text{pH}} + b_2 u_{\text{pH}}^2$

$u_{\text{E}}, \text{V}$	$b_0$	$b_1$	$b_2$	$R^2$
0.0001	0.00040	0.0200	0.0985	0.9979
0.0002	0.00020	0.0262	0.0388	0.9979
0.0004	0.00010	0.0273	0.0416	0.9995
0.0006	0.00004	0.0306	0.0131	0.9998
0.0010	0.00001	0.0319	0.0043	0.9999

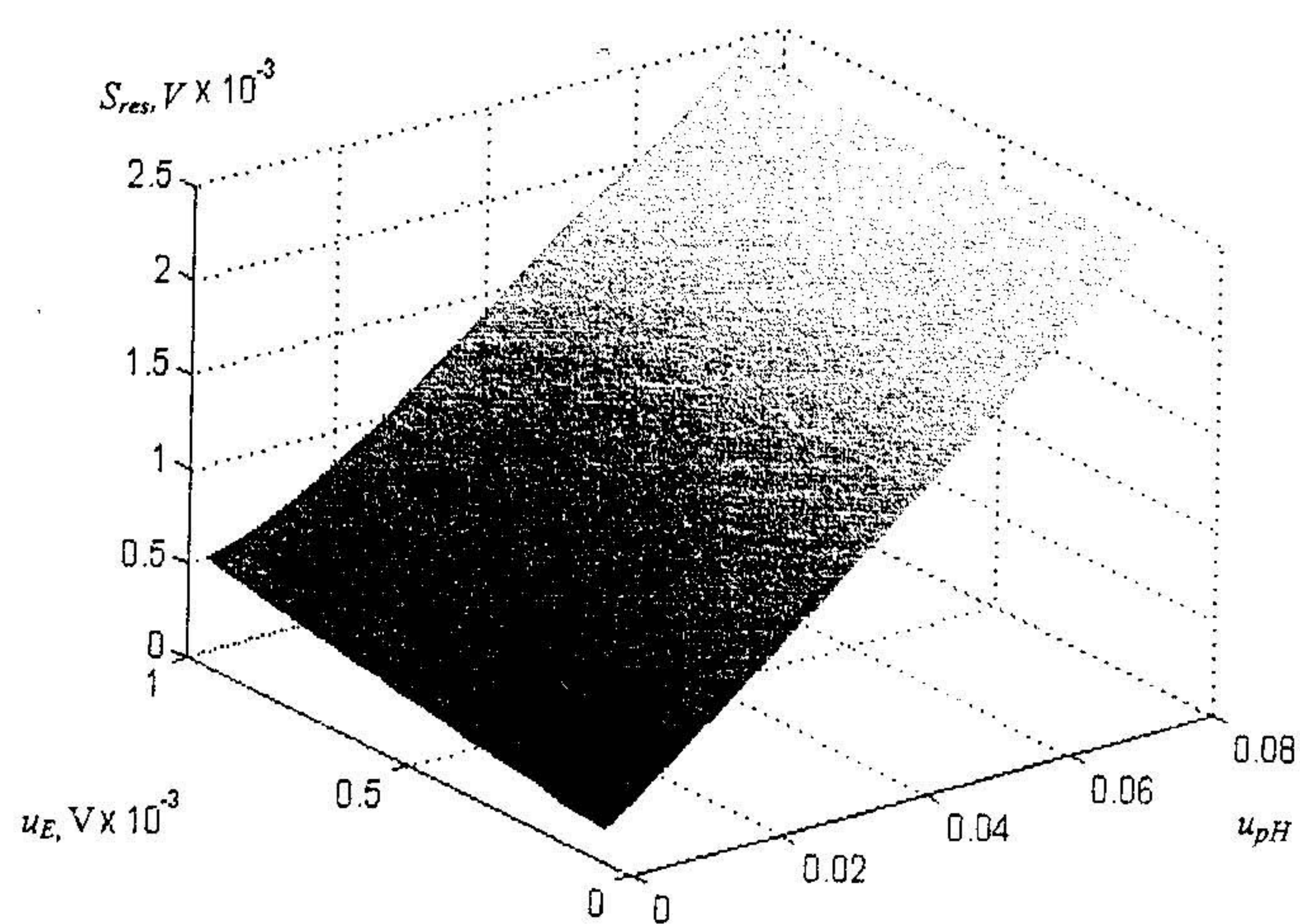


**Fig. 2** Dependence of the residual standard deviation  $S_{\text{res}}$  of a calibration curve on pH uncertainty of buffers  $u_{\text{pH}}$  at different instrumental uncertainties  $u_{\text{E}}$ .

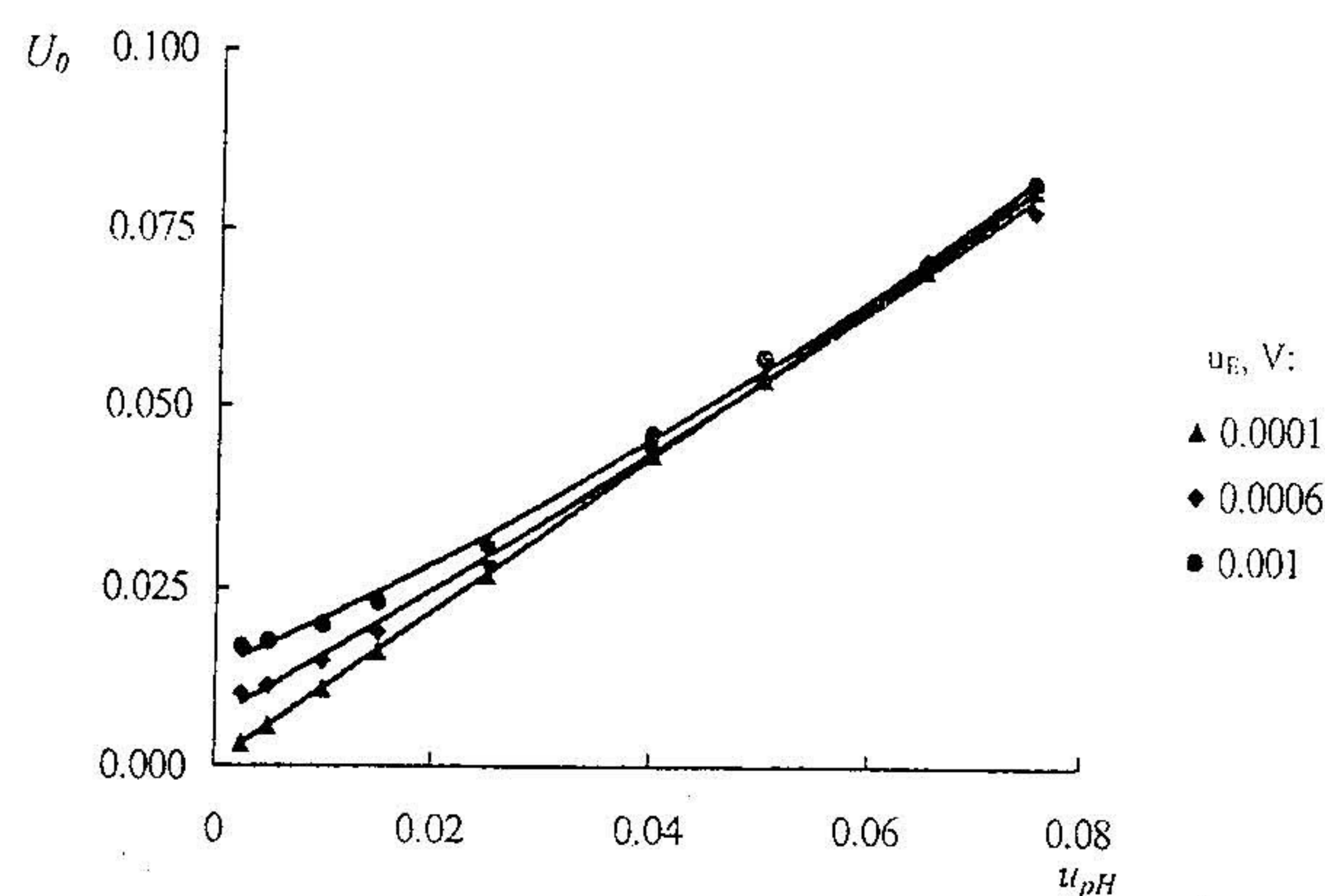
by the calibration, was evaluated by the following equation [5]:

$$u_0 = \frac{S_{\text{res}}}{b} \left\{ \frac{1}{n} + \frac{1}{m} + \frac{(E_0 - E_{\text{av}})^2}{b^2 \sum_i (\text{pH}_{\text{cert}}^i - \text{pH}_{\text{av}})^2} \right\}^{1/2}, \quad (8)$$

where  $E_0$  is the experimental value of electromotive force from which the value  $\text{pH}_0$  is to be determined, and  $m$  is the number of replicates. The confidence intervals calculated as expanded uncertainties  $U_0 = t u_0$  ( $t$  is the Student's coefficient for  $n-2=4$  degrees of freedom and 0.95 level of confidence) are in the same dependence on  $u_{\text{pH}}$  as the residual standard deviation  $S_{\text{res}}$  (see Fig. 4). The lines of equal confidence intervals  $U_0$  for the range of



**Fig. 3** Three-dimensional dependence of residual standard deviation  $S_{\text{res}}$  of a calibration curve on pH uncertainty of buffers  $u_{\text{pH}}$  and on instrumental uncertainty  $u_{\text{E}}$ .



**Fig. 4** Dependence of confidence intervals  $U_0$  for results of pH measurements in a sample under analysis (with  $\text{pH}_0 = 6.8$ ) on pH uncertainty of buffers  $u_{\text{pH}}$  at different instrumental uncertainties  $u_{\text{E}}$ .

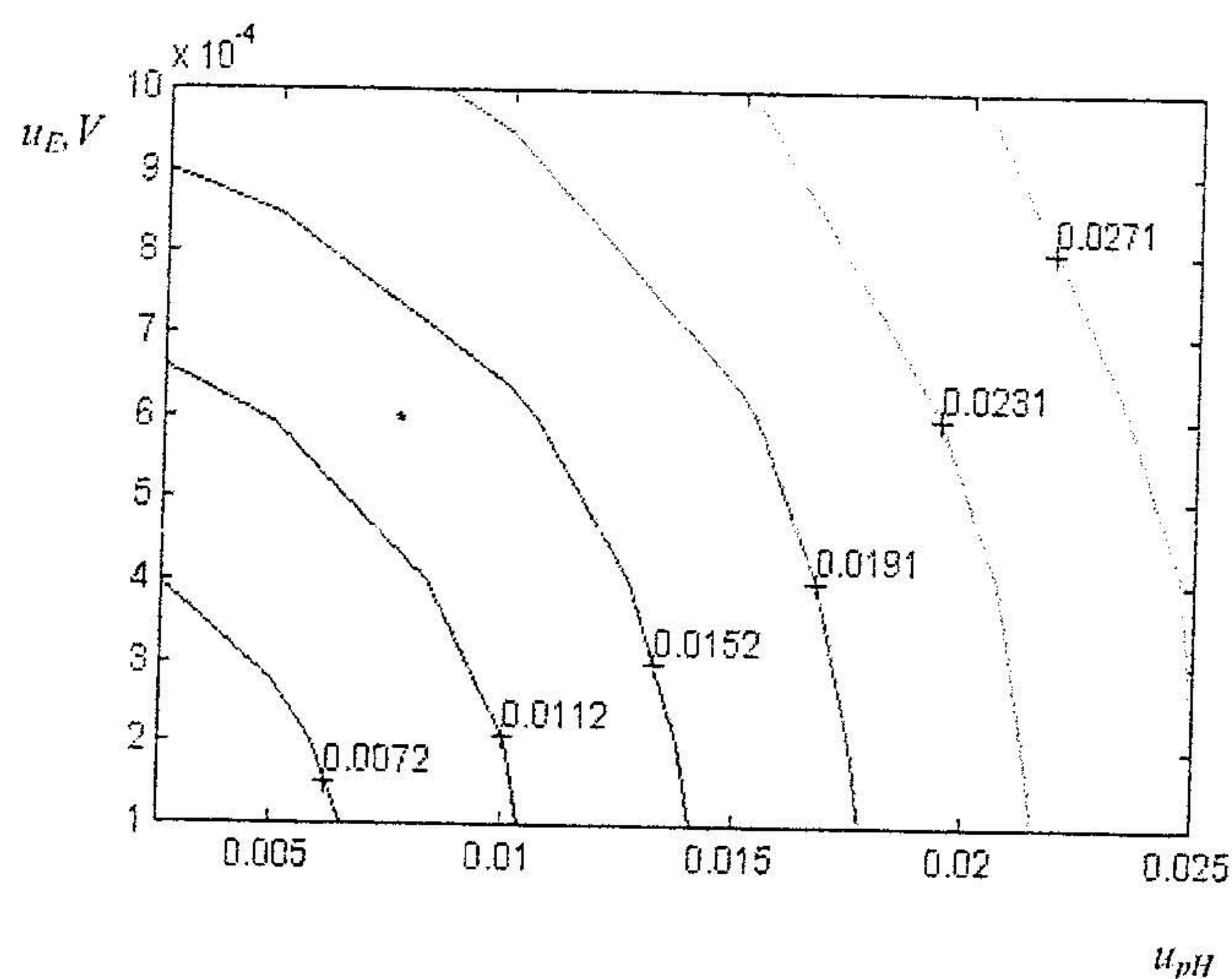


Fig. 5 The lines of equal confidence intervals  $U_0$  for  $\text{pH}=6.8$  at different  $\text{pH}$  uncertainties of buffers  $u_{\text{pH}}$  and instrumental uncertainties  $u_E$ .

$\text{pH}$  uncertainties of buffers  $u_{\text{pH}}=0.0025\text{--}0.025$  and for the range of instrumental uncertainties  $u_E=0.0001\text{--}0.001$  V are shown in Fig. 5. Though the influence of the instrumental uncertainty on  $U_0$  is minimal, the use of a less precise  $\text{pH}$ -meter (if  $u_E=0.001$  V instead of  $u_E=0.0001$  V) with high precision buffers ( $u_{\text{pH}}=0.0025$ ) leads to the increase of the confidence intervals by more than two-fold.

## Experimental

In order to assess the prediction results, three replicate calibrations of two  $\text{pH}$ -measurement systems with different instrumental uncertainties (a system for routine  $\text{pH}$  measurements with a glass electrode, and a system for high precision  $\text{pH}$  measurements with a hydrogen electrode) were performed using three sets of buffers with different uncertainties of certified  $\text{pH}$  values.

### Apparatus

The measurement system for routine analysis consisted of a working glass electrode 6.0133.100, a reference  $\text{Ag}/\text{AgCl}$ , 3 M  $\text{KCl}$ , 3 M  $\text{KNO}_3$  electrode 6.0726.100, and a  $\text{pH}/\text{ion}$ -meter Metrohm 744 with a standard uncertainty of 1 mV (Metrohm, Switzerland). The electrochemical cell with the electrodes was immersed in a constant temperature bath at  $25\pm 0.1$  °C.

The system for high precision  $\text{pH}$  measurements included a working hydrogen electrode, a reference  $\text{Ag}/\text{AgCl}$ , 3 M  $\text{KCl}$  electrode REF 321 immersed in the 3 M  $\text{KCl}$  bridge solution, and a  $\text{pH}/\text{ion}$ -meter PHM-240 with a standard uncertainty of 0.1 mV (Radiometer,

France). The hydrogen working electrode was prepared from a platinum wire (surface  $60\text{ mm}^2$ ) platinized for 2 min with a current density of  $60\text{ mA}\cdot\text{cm}^{-2}$  as a cathode in 2% chloroplatinic acid solution with addition of lead acetate (50 mg/l) [10]. Then it was activated in 0.5 M sulphuric acid for 2 min as a cathode, and for 8 min as an anode. The electrochemical cell with the electrodes was immersed in a constant temperature bath at  $25\pm 0.05$  °C.

### Reagents

The following sets of standard buffer reference materials were used:

- Merck, Germany, CertiPUR buffers with  $\text{pH}=3.00, 4.01, 5.00, 6.03, 6.99, 7.96$  and  $8.97$  at  $25$  °C; the expanded uncertainty of the certified values  $\pm 0.015$
- IUPAC  $\text{pH}$  standards from Radiometer, France, with  $\text{pH}=1.697, 4.005, 6.865, 7.000, 7.413, 9.180$  and  $10.012$ ; the expanded uncertainty  $\pm 0.01$
- Primary NIST SRMs with  $\text{pH}=3.557, 6.863, 7.416, 9.180, 10.011$ , the primary standard recommended by NIST [11] with  $\text{pH}=3.776$ ; the expanded uncertainty  $\pm 0.005$ .

Potassium chloride (99.99%) for preparation of the bridge solution and 8% chloroplatinic acid solution were from Aldrich, USA; 1 N sulphuric acid – from Merck, Germany. Hydrogen (99.999% – from a local company) was additionally purified from oxygen using a High-Capacity Indicating Oxygen Trap (Restec, USA).

## Results and discussion

Both measurement systems were calibrated 3 times, one per day. The values of the electromotive force measured using the hydrogen electrode were corrected for +1.6 mV to compensate the difference of the atmospheric pressure in Jerusalem and standard atmospheric pressure [12]. The standard residual deviations of calibration curves (three replicates for each set of buffers) are shown in Table 2. The dependence of the average values of these deviations on the uncertainty of buffers is close to the predicted one (the discrepancy is not more than 3 standard deviations of the experimental replicates from their means). However, the experimental values are systematically greater than the predicted deviations. The difference between the predicted and experimental values is caused, probably, by the uncertainty components that were not taken into account during the simulations, such as the memory effect of the electrodes, rate of hydrogen flow, etc. [9].

**Table 2** Predicted and experimental residual standard deviations  $S_{res}$  of calibration curves at different instrumental and buffers uncertainties

Instrumental uncertainty, mV	Producer of buffers	Uncertainty of buffers	$S_{res}$ , mV		
			Experimental		Predicted
			Replicates	Average	
0.1	NIST	0.005	0.18	0.25	0.17
			0.24		
			0.33		
	Radiometer	0.01	0.56	0.49	0.33
			0.38		
			0.52		
Merck	0.015	0.73	0.67	0.49	
		0.67			
		0.62			
1	NIST	0.005	0.42	0.44	0.30
			0.47		
			0.44		
	Radiometer	0.01	0.43	0.50	0.42
			0.41		
			0.68		
	Merck	0.015	0.61	0.73	0.55
			0.83		
			0.75		

## Conclusions

- Dependence of the uncertainty of a result of pH measurement in a sample under analysis on quality of buffers (uncertainty of their certified pH) for different levels of instrumental (pH-meter) uncertainty can be simulated by quadratic polynomials using the Monte Carlo method and regression analysis. This simulation allows one to optimize the choice of pH-meter and buffers in order to meet the required uncertainty of pH measurement result in a sample under analysis.
- The contribution of the instrumental uncertainty to the uncertainty of pH measurement result (caused by instrument calibration) is negligible if the standard uncertainties of the pH buffers exceed 0.04 pH (e.g. for in-house buffers).
- The results of the prediction based on the simulation are close to the experimental values obtained using commercial instruments and sets of buffers.

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