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THE QUALITY OF pH MEASUREMENT PROCESS

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ABSTRACT: The value of pH is an important quality control parameter measured in industry and research. The quality of the measurement process can be evaluated in the same manner as any manufacturing process. The aim of submitted work is to analyze the quality of pH measurement. MSA, analysis of uncertainty, t-test and ANOVA were used. Four appraisers measured pH of 10 solutions of HCl and HNO_3. The pH meter GRYF 208L with standard electrode THETA 90 HC 113 were used as measurement equipment. Analyzed the process of pH measurement is capable according to MSA. The fine discrimination and high accuracy of used equipment and high pH variability of measured solutions are reasons of high process capability. Low value of index %AV witness good competence of all appraisers. Positive effect of appraisers on the capability was confirmed by t-test and ANOVA.
KEYWORDS: measurement, pH, acids, capability, uncertainty

INTRODUCTION

The value of pH is an important quality control parameter used in metallurgy, chemistry, food processing, pharmaceutical production and environmental control. It is commonly measured by calibrated pH meters.

It is one of the most frequent and relatively simple measurement methods. Like in any test of material properties, there is an obvious requirement for reliability of measurement results, which is unthinkable without sufficient quality of the measurement process.

The quality of the measurement process can be evaluated in the same manner as any manufacturing process. The measurement process takes place in the measurement system. The aim of the measurement system in accordance with the standard STN EN ISO 10012:2004 [1] is to regulate hazard that the measurement equipment or measurement process could provide incorrect results. Incorrect results negatively affect the final quality of products followed by economic or moral damages (e.g. the loss of producer's image).

Although, from experience, we can suppose that confirmed measurement equipment will still be accurate at the end of confirmation status, there is an obvious danger of equipment misuse. The misuse can result from incorrect measurement method, measurement environment or incompetent appraisers.

Metrological confirmation comprises measuring equipment calibration and verification. Metrological confirmation shall be designed and implemented to ensure that the metrological characteristics of the measuring equipment meet the metrological requirements for the measurement process [1].

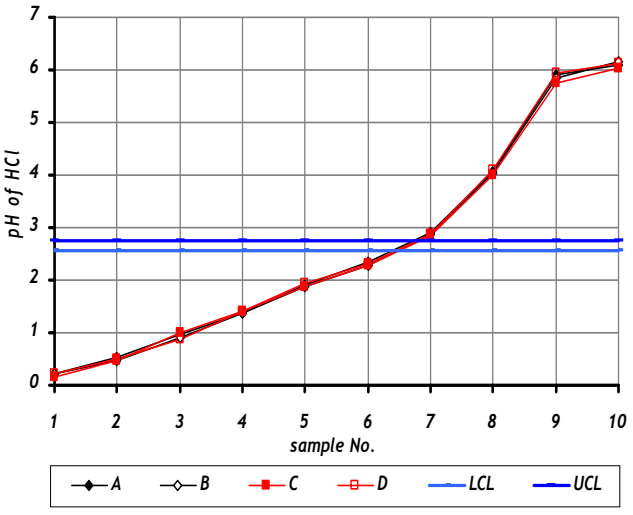

Figure 1.a: The average control chart, HCl

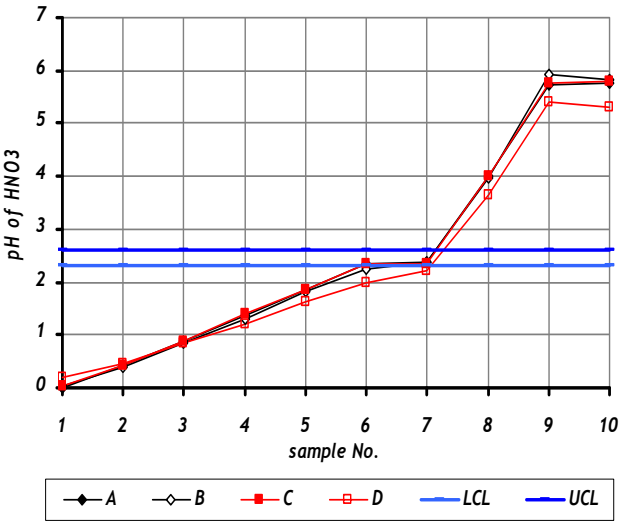

Figure 1.b: The average control chart, HNO3

Calibration is a set of operations that establish, under specified conditions, the relationship between values of quantities indicated by a measuring instrument or measuring system and the corresponding values realized by standards (certified reference materials CRM, buffers)[2].

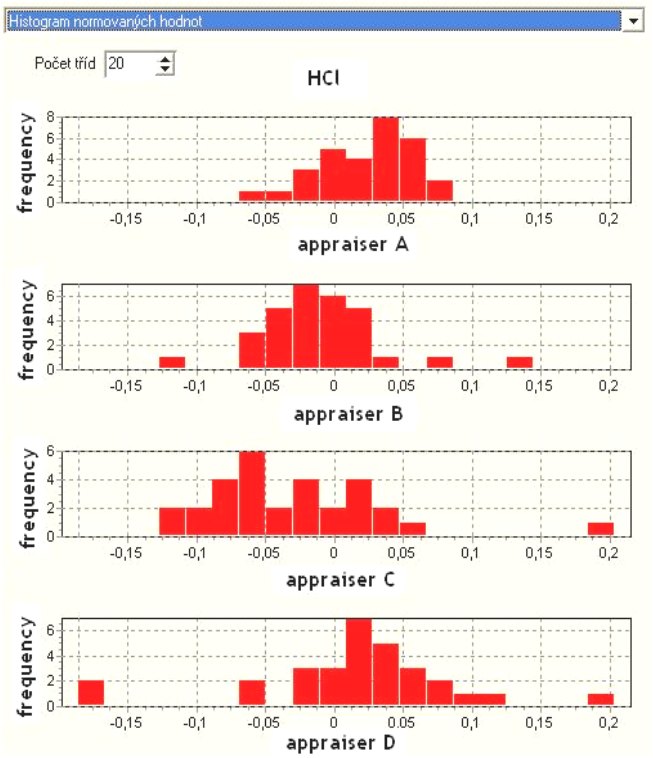

Figure 2.a. The normalized histogram, HCl

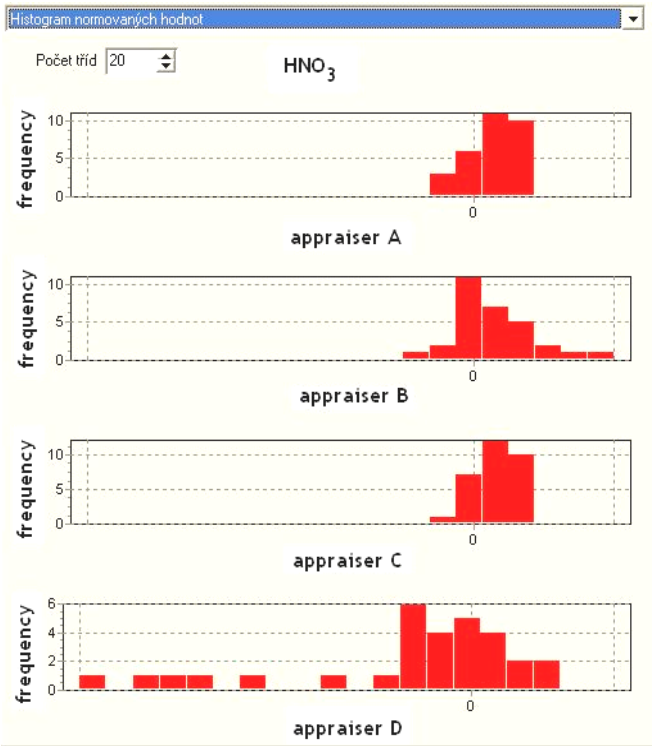

Figure 2.b. The normalized histogram, HNO_3

A perfect measurement would provide the true value of a quantity; nevertheless the true value is indeterminable in reality because a perfect measurement cannot be performed. The estimation of the true value is the finally corrected result. The measurement uncertainty is a parameter that characterizes the dispersion of the values that could reasonably be attributed to the result of measurement. Testing laboratories shall have and shall apply procedures for estimating uncertainty of measurement or calibration [3].

The aim of submitted work is to analyze the quality of pH measurement of water solutions of two acids (HCl and HNO_3) by evaluation of the measurement process capability by MSA method and by analysis of uncertainty. The results were validated using t-test and analysis of variance (ANOVA).

EXPERIMENTAL

The pH of ten samples with various HCl and HNO_3 concentrations prepared in agreement with calculation (calculated pH in Table 1 and Table 2) was measured by routine method by four appraisers (A, B, C, D) in 3 trials.

Table 1.a. The values of "measured pH", the standard deviation SD, statistical standard uncertainty u_A, normality, outliers and the error of repeatability r_{rel}. The values of pH, HCl.

	1	2	3	4	5
calculated pH	0	0.5	1.0	1.5	2.0
measured pH	0.198	0.489	0.947	1.383	1.908
SD of measured pH	0.039	0.042	0.085	0.041	0.039
u_A (n = 12)	0.011	0.012	0.025	0.017	0.011
normality (p)	0.076	0.369	0.014	0.323	0.418
outliers	1	0	0	0	0
r_{rel} (%)	75.6	24.5	40.1	9.4	5.8
	6	7	8	9	10
calculated pH	2.54	2.84	4.0	6.0	6.0
measured pH	2.307	2.875	4.045	5.863	6.111
SD of measured pH	0.039	0.073	0.057	0.100	0.071
u_A (n = 12)	0.011	0.021	0.016	0.029	0.021
normality (p)	0.052	0.106	0.513	0.526	0.214
outliers	0	1	0	0	0
r_{rel} (%)	4.8	9.4	4.4	5.3	3.8

Table 1.b. The values of "measured pH", the standard deviation SD, statistical standard uncertainty u_A, normality, outliers and the error of repeatability r_{rel}. The values of pH, HNO_3.

	1	2	3	4	5
calculated pH	0	0.5	1.0	1.5	2.0
measured pH	0.646	0.142	0.583	1.242	1.904
SD of measured pH	0.093	0.044	0.075	0.108	0.158
u_A (n =12)	0.027	0.013	0.022	0.031	0.046
normality (p)	0	0.004	0	0	0
outliers	0	1	1	1	1
r_{rel} (%)	40.3	41.0	35.0	31.3	32.1
	6	7	8	9	10
calculated pH	2.54	2.84	4.0	6.0	6.0
measured pH	2.288	2.333	3.942	5.708	5.675
SD of measured pH	0.217	0.069	0.237	0.267	0.302
u_A (n =12)	0.063	0.020	0.068	0.077	0.087
normality (p)	0	0	0	0.002	0
outliers	1	0	2	1	3
r_{rel} (%)	33.2	9.0	21.7	19.1	19.2

The pH meter GRYF 208L (the range of measurement 0-14 pH, range of adjustment N (for pH 7) ± 1.8 pH, range of adjustment S (for pH 4) ± 0,8 pH, the accuracy of measurement ± 0.01 pH ± 1 dig. with

standard electrode THETA 90 HC 113 were used as measurement equipment. The equipment was in accordance with standard STN 99 9000:1997 [4]. Two working buffers - reference materials with a nominal value pH 7 and pH 4 were used for calibration. The temperature of samples varied in range 24.1-26.1°C for HCl and 26.2-27.5°C for HNO_3. The temperature 25°C was designated for adjustment and calibration of equipment.

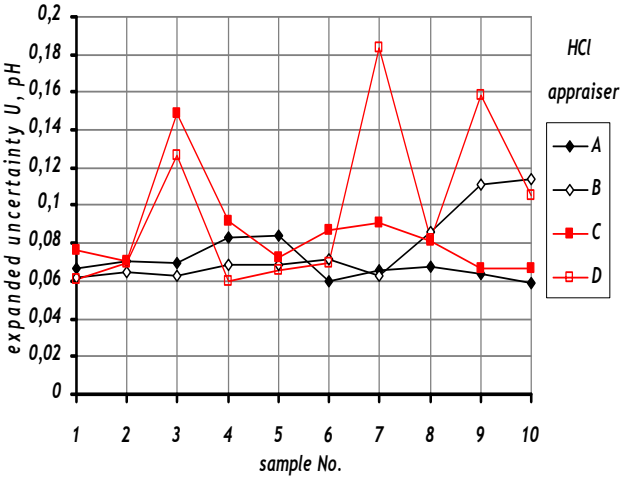

Figure 3a. The expanded uncertainty U of particular appraisers, HCl

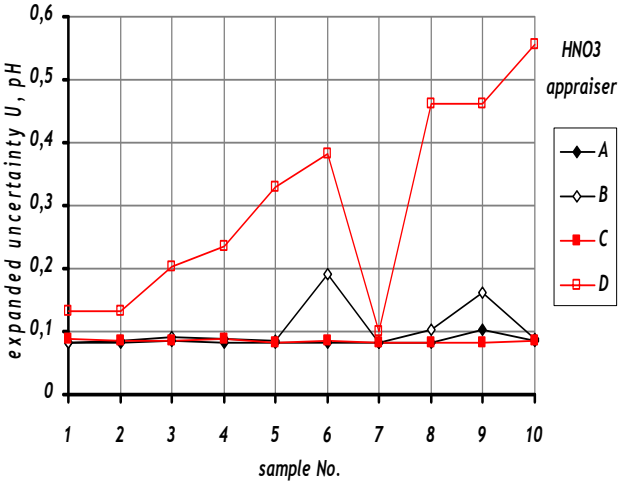

Figure 3b. The expanded uncertainty U of particular appraisers, HNO_3

The Measurement Systems Analysis (MSA) was originally designed for the engineering industry. If is used outside its intended scope - in chemical analysis, it is needs to regard the peculiarities of both areas with a different approach, traditions and object of interest (the part in engineering - a solution in chemistry).

MSA is not standardized yet but is recommended in the reference manuals for the automotive industry. It helps to conform with ISO/TS 16 949:2009 [5] requirements, as well as AIAG standards. MSA is an experimental and mathematical method of determining how much the variation within the measurement process contributes to the overall process variability. If the analyzed measurement system (consists of measurement equipment, parts, environment, method, appraisers…) is capable, it is likely that the measurement process, taking place in it is capable, as well. The capability is the ability of the system or process to realize a product that will fulfill the requirements for that product.

The analysis of variance (ANOVA) is one of MSA methods. Its advantages are that it is capable of handling any experimental set-up, can estimate the variance accurately and extracts more information from the experimental data. The disadvantages are the complex numerical computations and users required to have a certain degree of statistical knowledge to interpret the results. Simpler method of MSA, GRR (gauge repeatability and reproducibility) is an approach which will provide an estimate of both repeatability and reproducibility for a measurement system.

This approach will allow the measurement system's variation to be decomposed into two separate components, repeatability and reproducibility. However, variation due to the interaction between the appraiser and the part/gage is not accounted for in the analysis [6].

The calculation of capability by GRR method was carried out in accordance with [6] using the software Palstat CAQ (significance level α = 0.01 and confidence level α = 0.01 ≈ 5.15 σ).

The uncertainty of measured pH values was calculated in accordance with the standard [4]

$$u = \sqrt{u_A^2 + u_{\Delta s}^2 + u_{\Delta pHi}^2 + u_z^2} \qquad (1)$$

The values in Table 1 are the results of all 3 trials of all 4 appraisers (number of measurements n = 12). The "measured pH" is the average value of 3 trials of all 4 appraisers, "SD of measured pH" is the standard deviation of 3 trials of all 4 appraisers. The first source of uncertainty is statistical uncertainty u_A, calculated by formula (2); n = 3 for 3 trials of particular appraiser or n = 12 for 3 trials × 4 appraisers.

$$u_A = \frac{SD}{\sqrt{n}};\ n = 12 \qquad (2)$$

$u_{\Delta s}^2$ *- function of the difference between the measured value of pH and value of pH of calibration*

$$u_{\Delta s}^2 = \frac{\Delta s(\ pH - pH_s\ )}{s \cdot \chi} \qquad (3)$$

$\Delta s, s$ *- functions of temperature, listed in the standard [4]*

pH *- average pH (3 trials)*

pHi *- pH of certified reference material (buffer)*

$\chi = \sqrt{3}$ *for assumed rectangular distribution.*

$$u_{\Delta pHi} = \frac{\Delta pHi\,\alpha(t - \Theta)}{s \cdot \chi} \qquad (4)$$

$\Delta pHi \approx 4$ *for ordinary pH-meter and glass electrode*

α = 0.1984 mVK^{-1}

t *- temperature of measurement*

Θ *- temperature of calibration*

s *- function of temperature, listed in standard, [4]*

$\chi = \sqrt{3}$ *for assumed rectangular distribution.*

The source of uncertainty that is not specified in the standard [4] is connected with discrimination (resolution) δ_z = 0.01 pH of used pH meter [7].

$$u_z = \delta_z \cdot 2\sqrt{3} = 0.29\delta_z \quad (5)$$

The effort devoted to determining other eventual sources of measurement uncertainties was proportional to the importance of the measurement results. Their detailed determination is unjustifiable on technical grounds.

Expanded uncertainty

$$U = u \times k \quad (6)$$

The coverage coefficient k = 2

The uncertainties and coverage factors could be calculated using other methods [7], as well.

r_{rel} is relative repeatability (the error of repeatability)

$$r_{rel} = \left(\frac{pH_{max} - pH_{min}}{AVER} \right) \times 100\% \quad (7)$$

RESULTS AND DISCUSSION

The error of repeatability is inversely proportional to pH. The value of error for HNO_3 is higher than that for HCl.

The normality was determined by Freeware Process Capability Calculator software, using Anderson - Darling test ($p \geq 0.07$ for a file with a normal distribution). The standard methods of MSA assume normal probability distribution. If normality of the file is not confirmed, the measurement system error is overestimated. The statistical outliers would indicate that the process is suffering from special causes (disturbances) and is out of statistical control.

The normality and the outliers were evaluated for files, involving the results of all measurements of one sample (n = 12). On one hand, all files of HCl have a normal distribution an only two files contain outliers; on the other hand, the normality was not confirmed for all files of HNO_3 and eight samples contained 1-3 outliers (Table 1, Table 2).

The first step of MSA is the analysis of the equipment resolution - to estimate whether the discrimination (the value of the smallest scale graduation of equipment) is sufficient.

A general rule of thumb is that the discrimination ought to be at most one tenth of the process variation [6]. If we compare the value of discrimination δ_z = 0.01 pH with values of standard deviation ("SD of measured pH", Table 1), the resolution of used equipment is terminal.

The measurement system ought to be under statistical control before capability is assessed. The process is under control if all ranges are between control limits of the range control chart. If one appraiser is out of control, the method used differs from the others (appraiser D). The average control chart (X-bar control chart) provides an indication of "usability" of the measurement system. The area within the control limits represents the measurement sensitivity ("noise"). If one half or more of the averages falls outside the control limits, then the measurement system should be considered adequate to detect variation between the levels of pH. Analyzed system has sufficient sensitivity - all measurements for HCl and 87.5 % measurements for HNO_3 are outside the control limits (Figure 1).

Table 2. a. The paired t-test comparing the means of two groups - the average value of pH measured by particular appraiser and "measured pH" - average value of 4 appraisers.HCl, p - values.

appraiser	1	2	3	4	5
A	0.2546	0.0912	0.6176	0.7193	0.6473
B	0.8319	0.2212	0.6038	0.372	0.3415
C	0.06	0.3393	0.2691	0.7313	0.4954
D	0.4387	0.0001	0.2548	0.3508	0.2474
	6	7	8	9	10
A	0.3367	0.5346	0.4524	0.3591	0.7357
B	0.6013	0.9477	0.7533	0.6412	0.2241
C	0.2886	0.6896	0.1374	0.1075	0.1199
D	0.4315	0.8373	0.2667	0.2774	0.5933

Table 2. b. The paired t-test comparing the means of two groups - the average value of pH measured by particular appraiser and "measured pH" - average value of 4 appraisers. HNO_3, p - values.

appraiser	1	2	3	4	5
A	0.2649	0.9259	0.5607	0.4153	0.4413
B	0.018	0.3188	0.6151	0.8693	0.7061
C	0.5087	0.8785	0.6364	0.3642	0.5145
D	0.0145	0.4109	0.6854	0.2185	0.1608
	6	7	8	9	10
A	0.3508	0.3245	0.4939	0.8452	0.6057
B	0.9248	0.3261	0.6171	0.1926	0.3943
C	0.4172	0.5763	0.4797	0.7494	0.5226
D	0.1317	0.0265	0.1362	0.1271	0.1123

Table 3. A paired t-test comparing the means of two groups - the average value of pH measured by particular appraiser, p values.

appraiser	HCl			HNO_3		
	A	B	C	A	B	C
B	0.0496	-	-	0.8832	-	-
C	0.0165	0.3280	-	0.5377	0.8376	-
D	0.6625	0.1048	0.1046	0.0170	0.0322	0.0179

The number of distinct categories ("ndc", based on Wheeler's discrimination ratio) is connected with the resolution of equipment. It indicates the number of various categories, which can be distinguished by the measurement systems. It is the number of non-overlay 97 % confidence intervals, which cover the range of expected variability of product.

The ndc ≥ 5 for capable processes, the processes with ndc between 2-5 may be conditionally used for rough estimations. Ndc for HCl is 48.6 and for HNO_3 is 20.5. Value of ndc and analysis of the average control chart demonstrate sufficient sensitivity of the measurement system for variability of measured value.

%EV index represents cumulative influence of measurement equipment, measuring method and environmental conditions on the variability. It is a function of average range of trials of all appraisers. The value of %EV is 2.69 % for HCl and 4.9 % for HNO_3.

Whereas standardized measurement method and equipment with valid confirmation status were used,

only the resolution of equipment and the environment (variation of ambient temperature) could affect the value of %EV index.
%AV index represents the influence of appraisers on the variability. It is a function of the maximum average appraiser difference. The value of %AV is 1.15 % for HCl and 4.78 % for HNO_3. Low value of index confirms competence of appraisers.
%GRR index represents the process capability in practice. For acceptable measurement system %GRR < 10 %, %GRR > 30 % is considered not acceptable.
Analyzed measurement system and also the process carried out within it are acceptable - capable because %GRR is 2.90 % for HCl and 6.85 % for HNO_3.
%PV index is a function of the range of the pH values of particular samples. It is sensitive to variability between samples pH. The value of %PV indirectly defines suitability of equipment for specific measurement. %PV above 99 % suggests extremely accurate, above 90 % suitable, above 70 % satisfactory and above 50 % inaccurate equipment. Because %PV is 99.96 % for HCl and 99.77 %, for HNO_3, used equipment is extremely accurate for both acids in respect of variability between the pH of samples.
Normalized histogram - histogram plot is a graph that displays the frequency distribution of the gage error of appraisers who participated in the study.
The graph provides a quick overview how the error, i.e. difference between an observed value and reference value (samples average) is distributed. As can be seen in Figure 2a, the differences of bias (systematic error - the difference between the peak of histogram peak and zero) and variability (random error - the width of histogram) between appraisers for all measurements are negligible for HCl. The results of appraiser B have minimum variability and are best centered. As can be seen in Figure 2b, the differences between appraisers A-B-C are low, the variability of appraiser D is superior to others in the measurement of HNO_3.
As far as the analysis of uncertainty, the relation between the average value of pH and expanded uncertainty U of the result is ambiguous and depends on appraisers, Figure 3. The uncertainty moderately increases with increasing of "measured pH" (Table 1) for appraises B, D and decreases for appraisers A, C in measurement of HCl. It also moderately increases with increasing of "measured pH" for appraises A, B, C and intensively increases for appraiser D in measurement of HNO_3.
A paired t-test comparing the means of two groups (significance level $\alpha = 0.01$) was used for evaluation of particular appraisers quality e. i. difference between the values of particular appraiser and "measured pH" - average value of 4 appraisers (Table 1). The difference is statistically significant for $p \leq 0.05$. Table 2 summarizes that except for one sample of HCl (appraiser D) and three samples of HNO_3 (two appraiser D, one appraiser B) the differences were not statistically significant. It confirms low value of %AV index as well as low difference between competence of particular appraisers.
The comparison of the average pH values of particular appraisers by paired t-test (3 trials, all samples) are in Table 3. The differences are statistically significant between appraisers A-B and A-C are for HCl and between appraiser D and others appraisers for HNO_3.
According to a single factor analysis of variance (ANOVA) the influence of appraiser on the measured values of pH is not statistically significant for both acids ($p = 0.9999$ for HCl and 0.9955 for HNO_3).
Four appraisers measured the pH of distilled water H_2O and five water solutions: hydrochloric acid HCl, sodium hydroxide NaOH, sodium bicarbonate $NaHCO_3$, acetic acid CH_3COOH and citric acid $C_6H_8O_7$ by routine method in accordance with standard [4], the capability of the process was comparable to abovementioned results (%GRR = 6.44 %) [8].
The capability of pH measurement is better than that of comparable measurement processes as a rule. For example, measurement process of foundry sand properties (compression strength RC2, shearing strength RT2 and mold permeability) was analyzed. It was capable of permeability (%GRR = 7.47 %) but not acceptable for RC2 (%GRR = 37.9 %) and conditionally acceptable for KT2 (%GRR = 23.49 %) [9].

CONCLUSIONS

1. Analyzed process of pH measurement is capable of both acids.
2. The fine discrimination (scale interval) and high accuracy of used equipment, high pH variability of measured solutions are reasons of high process capability.
3. Low value of index %AV proves good competence of all appraisers.
4. The influence of final pH and appraiser on expanded uncertainty of the results of measurement is inexpressive.
5. The t-tests and ANOVA confirmed minor influence of appraiser on the result of measurement.
6. The results of appraiser D show some distance from the results of others appraisers.
7. The lower capability of the measurement process of HNO_3 can be affected be other than normal probability distribution of the results.

ACKNOWLEDGEMENTS

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