

ARTICLES

# A Test Method for Determining Total Metals with an Indicator Paper and Its Performance Characteristics

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**Abstract**—A test procedure is proposed for determining total metals (Cd, Co, Cu, Fe, Hg, Ni, and Zn) using irregular 1-(2-carboxyphenyl)-5-(4-methyl-6-methoxypyrimidine-2-yl)formazan-6-cellulose as an indicator paper. Regions of unreliable color reactions were determined for each of the metals and total metals present in equal concentrations. Statistical processing showed that the Weibull distribution function best describes the experimental results in the unreliable reaction regions. Unreliable reaction was observed in the range  $(3.6\text{--}4.4) \times 10^{-3}$  mg/L for the test procedure with preconcentration and in the range 1.7–3.4 mg/L for the procedure without preconcentration; the detection limits are  $4.4 \times 10^{-3}$  and 3.4 mg/L, respectively. A synergetic effect of the component mixture was observed in determining total metals. The visual, reflectometric, and atomic absorption determination of total Co, Cu, Fe, Ni, and Zn in natural and tap water was studied; it was shown that the results of test determination agree well with the data of other methods.

The quality of natural, process, waste, and potable waters can be rapidly assessed using integral parameters, such as hardness, pH, acidity, alkalinity, chemical and biological oxygen demands, total heavy metals, total carbon, etc. [1]. Test methods for the reliable determination of groups of related contaminants at the level of their maximum permissible and hazardous concentrations have been developed insufficiently well: it is often unknown whether the contributions of the contaminants to the result of analysis are equal.

Some test methods were proposed for determining total heavy metals with reagent indicator papers (RIBs) [2–6] using the kinetic method [4], ion exchange with polydentate celluloses [2, 3], and reactions with poorly soluble reagents [6]. Each test reagent has advantages and disadvantages, such as low selectivity, insufficient contrast and homogeneity of color transitions, limited resistance to external impacts, and low stability upon storage. The development of new tests for the rapid determination of toxic metals requires new methodological approaches, including objective criteria for assessing the determination limit of related components and their sums.

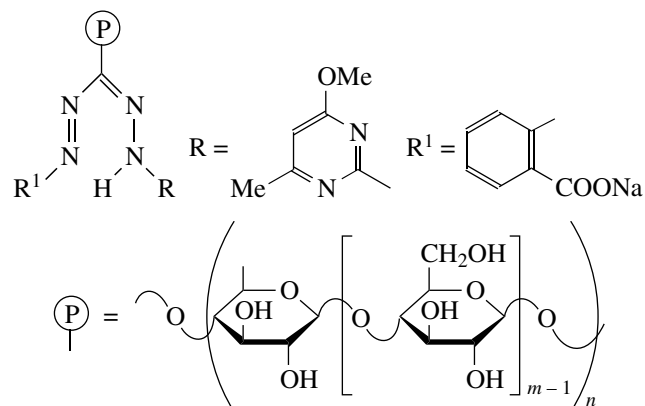
In this work, a visual test method was proposed for determining total Cd, Co, Cu, Fe, Hg, Ni, and Zn using RIB-Metall-Test II indicator strips [2] based on irregular cellulose bearing fragments of 1-(2-carboxyphenyl)-5-(4-methyl-6-methoxypyrimidine-2-yl)formazan sodium salt in position 6 of the glucopyranoside ring and its performance characteristics were studied. RIB has valuable properties, such as irregular structure (most of potentially tetradentate groups with chromophore and ion-exchange properties are concentrated

on the RIB surface, on which ion-exchange processes with color transitions occur); the formation of strongly colored complexes with heavy metals, which ensures the preconcentration of trace metals; the mechanical strength of RIB in the course of pumping liquid samples; stability upon storage (properties remain stable for more than 5 years while stored under standard conditions); the possibility of analyzing colored and turbid liquids and washing reaction products from colored impurities with ethanol or acetone without altering the color of the reaction zone; easy regeneration; and the feasibility of determination at pH 6–8 because of the buffer capacity of the reagent itself.

## EXPERIMENTAL

### Reagents and Apparatus

#### RIB-Metall-Test II



**Table 1.** Color and reflectometric characteristics of RIBs in test analysis without preconcentration

Ion, GSO	Color	$\sigma$ (%)* for $c$ , mg/L				
		0	50	100	200	500
Cu <sup>2+</sup> , 6073-91	Blue	0	20	30	50	70
	Purple	40	20	20	20	20
	Yellow	90	70	60	50	30
	Black	0	10	15	25	25
	$R_0, R_i$	126	90	77	70	43
Co <sup>2+</sup> , 8089-94	Blue	0	20	30	50	70
	Purple	40	20	20	20	20
	Yellow	90	70	60	50	30
	Black	0	10	15	25	25
	$R_0, R_i$	156	143	111	95	86
Cd <sup>2+</sup> , 5222-90	Blue	0	20	30	50	70
	Purple	40	20	20	20	20
	Yellow	90	70	60	50	30
	Black	0	10	15	25	25
	$R_0, R_i$	119	109	107	95	76
Zn <sup>2+</sup> , 5237-90	Blue	0	10	20	30	50
	Purple	40	40	50	70	70
	Yellow	90	80	70	50	30
	Black	0	0	15	15	15
	$R_0, R_i$	154	128	64	53	40
Fe <sup>3+</sup> , 6068-91	Blue	0	10	20	30	40
	Purple	40	40	40	40	50
	Yellow	90	80	70	60	50
	Black	0	0	0	15	15
	$R_0, R_i$	147	101	97	91	75
Ni <sup>2+</sup> , GOST 4212-76	Blue	0	10	30	55	80
	Purple	40	40	50	70	80
	Yellow	90	80	60	40	20
	Black	0	10	15	20	25
	$R_0, R_i$	151	145	141	120	66
Total Cd, Co, Cu, Fe, Hg, Ni, and Zn	Blue	0	20	30	50	70
	Purple	40	20	20	20	20
	Yellow	90	70	60	50	30
	Black	0	10	15	25	25
	$R_0$ or $R_i^{**}$	145	117	99	87	64

\*  $\sigma$  (%) denotes color chart gradations (TU 29.01-91-83).

\*\*  $R_0$  and  $R_i$  denote the diffuse reflectance of RIB and its compounds with metals, respectively, measured at 625 nm.

The degree of polymerization is  $n = (2000 - 16000)/m$ ;  $m = 10 - 300$ .

RIB is a uniform light yellow paper. The IR spectrum of the surface RIB layer exhibits broad bands with

a shoulder at 1590 and 1565  $\text{cm}^{-1}$  typical of the stretching vibrations of the  $\gamma_{\text{C=N}}$  groups of heterocyclic hydrazones and formazanes [3]. Reflectance spectra were recorded on a Perkin-Elmer 1760X FT-IR spectrophotometer (number of scans 132, resolution 8  $\text{cm}^{-1}$ ). The batch exchange capacity of RIB with respect to  $\text{Cu}^{2+}$  was 0.055 mmol/g. The RIB was cut into strips 10  $\times$  40 mm in size. The colors and reflectometric parameters of RIB complexes of metal ions are shown in Table 1.

**Solutions and apparatus.** A series of reference solutions containing Cd(II), Co(II), Cu(II), Fe(III), Hg(II), Ni(II), and Zn(II) ions and their combinations with equal concentrations of metal ions were prepared according to the State Standard (GOST) 4212-76 or using GSO certified reference materials (Table 1). The absorption spectra of RIB-metal complexes (Fig. 1) were recorded in a 0.1-cm glass cell using 565 nm on a KFK-3 spectrophotometer. Diffuse-reflectance coefficients were determined in the cell of a Metalltest colorimeter-reflectometer with a light-emitting diode (565 nm). The atomic absorption determination of metals was performed on an AAS-IN spectrometer and an S-115 M spectrophotometer after preconcentration by evaporation.

**Test procedure.** Metal concentrations at pH 6–7 were determined in two modes, with and without preconcentration. In the former case, 3 mL of a test solution was pumped for 30 s through a paper reaction zone 6 mm in diameter to the chamber of a pocket indicator tool [3]; the zone color was compared with the reference color scale (0, 0.01, 0.02, 0.05, 0.1, 0.2, 0.5, 1 mg/L) after 5 min. In the latter case, a RIB strip was immersed into a test solution for 3 s and the strip color was compared with the concentration scale (0, 10, 20, 50, 100, 250, 500 mg/L) after air drying for 5 min.

The natural reference color scale was prepared by the reaction of RIB samples with reference metal solutions followed by the drying of RIB and impregnation with a saturated solution of paraffin in diethyl ether to imitate a wet scale. The metal concentrations in the solutions ( $c$ ) were increased in geometric progression with a common ratio of 2. Any range of metal concentration can be set by varying sample volume used for preconcentration.

The reference color scale of the comparator was offset printed using the color chart technique (TU 29.01-91-83, Table 1). Model measurements showed that the colors of the comparator scale coincide with those of the natural reference scale.

The performance characteristics of the test procedure were determined by the expert method: a group of 10–15 observers was asked whether a colored spot was seen or not against the original yellow RIB background.

**Statistical methods for assessing the results of tests.** The performance characteristics of tests using visual indication are the detection limit ( $c_1$ ) and the determination limit ( $c_{\text{min}}$ ). The visual indication of an

analyte is affected by random errors, and the probability of analyte detection ( $P$ ) depends on the analyte concentration [7]. To assess the  $c_1$  and  $c_{\min}$  values, the region of unreliable reaction is determined [7], where the probability of analyte detection varies in the range  $0 < P(c) < 1$ ; i.e., a positive result is obtained for some samples and a negative result is obtained for other samples. In the region of unreliable reaction, repeated measurements are carried out for  $J$  levels of analyte concentration and the detection frequency  $c_k$  is found for each concentration studied:

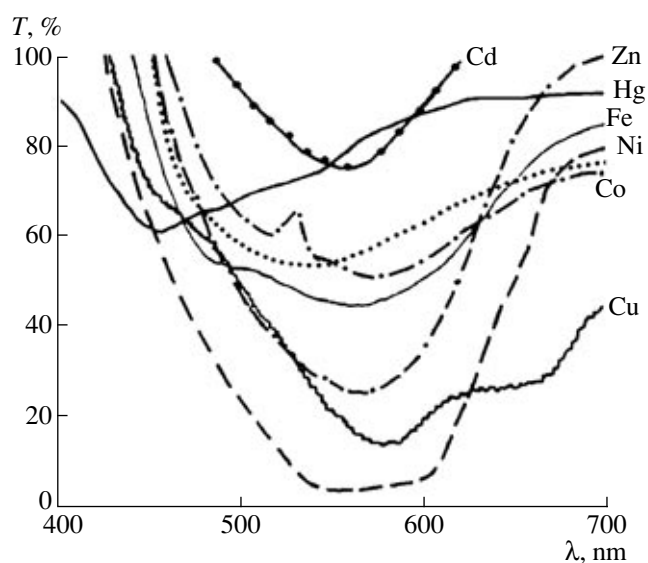
$$P(c_k) = \frac{n_k}{N_k}, \quad k = 1, 2, \dots, J, \quad (1)$$

where  $n_k$  is the number of observer's positive answers to the question about color appearance, and  $N_k$  is the total number of tests performed for concentration  $c_k$ .

In this work, the upper boundaries of the unreliable reaction region (i.e., concentrations detected by all observers) were taken as preliminary  $c_{\min}$  values for each metal and for the sum of equal metal concentrations. The  $c_{\min}$  values for total metals were refined in accordance with the recommendation that "in the analysis of pure substances, determination limit is calculated as the triple standard deviation of the result of determination of a near-limit concentration" [8]. To estimate standard deviation ( $s_c$ ), the color scale of the comparator was expanded to include the unreliable reaction region (every succeeding concentration was two times higher than the preceding one); metal concentrations in the model solutions were selected close to the preliminary  $c_{\min}$  values (so that they differ from reference concentrations of the color scale), and the observers estimated total metal concentrations in model solutions using the color scale. Each observer selected one of the three possible answers: the concentration of the test solution corresponds to the (a) upper, (b) lower, or (c) mean value in the range.

The detection limit was set equal to the analyte concentration for which  $P(c_1) = 0.95$ . The probability distribution function for the detection of metals in the unreliable reaction region and the parameters of this function should be known for calculating  $c_1$ . Komar' believed that distribution  $P(c)$  is described by the normal law [7]. Later on, other hypotheses were tested for some chromogenic reactions on reactive indicator papers, TLC plates, and inert supports [4, 5, 9–12]. The statistical verification of the nature of the distribution  $P(c)$  and the estimation of  $c_1$  were based mainly on limited numbers of experimental samples and involved the only parameter; the assessment for an integral parameter was reported only in [5].

In this work, the agreement between the empirical  $P(c_1)$  and theoretical distributions was studied for the normal, lognormal, Weibull, Poisson, and exponential



**Fig. 1.** Transmittance spectra of RIB-Metall-Test II compounds with metals (Cd, Zn, Hg, Fe, Ni, Co, and Cu) with respect to RIB at pH 6.0.

distributions (the last distribution is a special case of the Weibull distribution) (Table 2).

Graphical methods were proposed to test the hypotheses about some distribution laws [4, 5, 9–12]. The authors calculated the empirical frequencies of analyte detection and plotted  $P(c)$  as a function of  $c$  or  $\ln c$  (Table 2). If a nearly linear relationship was observed, the hypothesis about the agreement between the empirical and theoretical distributions was accepted. The unknown parameters of the distribution law were estimated from regression coefficients of the corresponding relationship [10]. Although graphical methods are most clear, they may be recommended for the preliminary assessment of distribution hypotheses. Thus, linear relationships cannot be obtained for all possible  $P(c)$  distributions and, second, numerical statistical estimates must be used to acquire objective information about the performance characteristics of tests. In addition, the application of the least-squares technique to linearized relationships in the calculation of distribution parameters violates the main prerequisites of this technique [14].

We added calculation and statistical methods to the graphical methods of validation with. The  $\chi^2$  criterion was proposed earlier for assessing the results of tests [9, 10]. In this work, it was supplemented with the Kolmogorov–Smirnov criterion and the calculation of sample skewness and kurtosis for the distribution of

weighted residues  $\Delta_k = \frac{\hat{P}(c_k) - P(c_k)}{s_k}$ , where  $\hat{P}(c_k)$

denotes the values of the distribution function calculated according to the studied law, and  $s_k$  is the standard deviation of  $P(c_k)$ .

**Table 2.** Studied distribution functions

Distribution law	Expression	Parameters	Linear dependence of
Normal	$P(c) = \frac{1}{\sigma\sqrt{2\pi}} \int_0^c \exp\left[-\frac{1}{2}\left(\frac{x-\bar{c}}{\sigma}\right)^2\right] dx$	$\bar{c}, \sigma$	$\Psi\{P(c)\}^*$ on $c$
Lognormal	$P(c) = \frac{1}{\sigma\sqrt{2\pi}} \int_0^c \exp\left[-\frac{1}{2}\left[\frac{\ln(x/\bar{c})}{\sigma}\right]^2\right] dx$	$\bar{c}, \sigma$	$\Psi\{P(c)\}$ on $\ln c$
Weibull	$P(c) = 1 - \exp\left(-\left(\frac{c-a}{b}\right)^k\right)$	$a, b, k$	$\ln \ln \frac{1}{1-P(c)}$ on $\ln c$
Exponential	$P(c) = 1 - \exp\left(-\frac{c-a}{b}\right)$	$a, b$	$\ln \frac{1}{1-P(c)}$ on $c$
Poisson	$P(c) = \int_0^c \frac{\bar{c}^x \exp(-\bar{c})}{x!} dx$	$\bar{c}$	

\* ( $\Psi$ ) inverse normal function [13].

The validation procedure using the criterion  $\chi^2$  included the following operations:

(1) The vector of the unknown parameters  $\{\theta\}$  was calculated for the studied distribution law:

$$|\theta\rangle = \arg \min \sum_{k=1}^J \frac{\{\hat{P}(c_k) - P(c_k)\}^2}{s_k^2}. \quad (2)$$

Kravchenko *et al.* [10] calculated standard deviations  $s_k$  as approximate asymptotic estimates [15]:

$$s_k \approx \sqrt{\frac{P(c_k)\{1 - P(c_k)\}}{N_k}}. \quad (3)$$

The  $s_k$  values can also be calculated in another way, if detection frequencies of the analyte in the statistical samples are known for each observer  $P(c_k)_i, i = 1, 2, \dots, I$ , where  $I$  is the total number of observers:

$$s_k = \sqrt{\frac{1}{I-1} \sum_{i=1}^I \{P(c_k)_i - \bar{P}(c_k)\}^2}. \quad (4)$$

Estimates (4) were higher than the values calculated by Eq. (3) by two to four times; i.e., the asymptotic estimates (3) were strongly underestimated. The  $s_k$  values calculated from Eq. (4) were used where possible. Functional (2) was minimized using the numerical simplex method and the conjugate gradients method. The distribution parameters found by different methods coincided, which was indicative of the attainment of the global minimum.

(2) From the found parameters, we calculated  $\hat{P}(c_k)$  and  $\chi_{\text{exp}}^2$

$$\chi_{\text{exp}}^2 = \sum_{k=1}^J \frac{\{\hat{P}(c_k) - P(c_k)\}^2}{s_k^2}. \quad (5)$$

The value  $\chi_{\text{exp}}^2$  was compared to the  $\chi_f^2$  ( $\alpha = 5\%$ ) – 5% point of the  $\chi^2$ -distribution with  $f = J - Z$  degrees of freedom ( $Z$  is the number of calculated distribution parameters). If inequality  $\chi_{\text{exp}}^2 < \chi_f^2$  ( $\alpha = 5\%$ ) was obeyed, it was concluded that the empirical distribution  $P(c)$  agreed with the studied theoretical distribution.

When the Kolmogorov–Smirnov criterion was used, the following test statistic was found:

$$\lambda_{\text{exp}} = \max_{1 \leq k \leq J} |P(c_k) - \hat{P}(c_k)| \sqrt{J}. \quad (6)$$

The difference between the empirical and theoretical distributions was considered significant when the probability of this value was  $P(\lambda) \leq 40\%$  [16].

In the analysis of distributions of weighted residues  $\Delta_k$ , skewness  $\tilde{A}$  and kurtosis  $\gamma_2$  were calculated (their mean values are zero when the empirical and theoretical distributions coincide). Although samples or larger size are necessary to test hypotheses about distributions using the sampled  $\tilde{A}$  and  $\gamma_2$  values compared to the usual number of concentration levels  $c_k$ , significant dif-

**Table 3.** Preliminary values of lower determination limit ( $c_{\min}$ ) and the unreliable reaction region ( $\Delta c$ ) for individual metal ions and their sum

Metal ion	$c_{\min}$ (mg/L)	$\Delta c$ , mg/L	Number of observations	Measurement procedure
Cu(II)	2.20	1.50–2.10	30	Without pre-concentration
Ni(II)	2.30	1.60–2.20	30	Same
Co(II)	3.00	1.50–2.75	30	"
Zn(II)	4.00	3.40–3.90	45	"
Cd(II)	19.0	18.5–19.0	30	"
Fe(III)	12.4	11.7–12.3	30	"
Hg(II)	100	80–110	30	"
Total	4.00	2.00–3.75	45	"
Total	$4.4 \times 10^{-3}$	$(3.5-4.3) \times 10^{-3}$	45	With preconcentration

ferences between the  $\tilde{A}$  and  $\gamma_2$  values and their expectations indicate that the hypothesis of coincidence between the theoretical and empirical distributions should be accepted with caution.

## RESULTS AND DISCUSSION

The preliminary values of the concentrations to be determined and the boundaries of unreliable reaction regions for each metal ion and total metals are listed in

Table 3. Similar values of  $c_{\min}$  and  $\Delta c$  were obtained for copper, nickel, cobalt, and zinc;  $c_{\min}$  was higher than  $\Delta c$  by five to six times for cadmium and iron and by 30 times for mercury. These results agree with the properties of human eye: blue is better perceived against the background of light yellow RIB compared to red–brown (the products of RIB interaction with metal ions are dark blue for Cu(II) and Ni(II); violet–blue for Zn(II); violet–brown for Cd(II), Co(II), Fe(II), and Fe(III); and brownish red for Hg(II). Taking into account that the concentrations of mercury and cadmium in natural water bodies and tap water are lower by two or three orders of magnitude and that the unequal contributions of metals to the determination of their sum deteriorate the determination error, the contributions of mercury and cadmium to the total signal may be ignored.

The results of the observations and the refined calculated values of  $s_r$  and  $c_{\min}$  ( $c_{\min} = 2s_r$ ) are shown in Table 4. The preliminary  $c_{\min}$  values for total metals virtually coincided with the calculated values (Table 3, 4).

In the proposed test method, the determination limit for total metals ( $c_{\min} = 4.00$  mg/L) was only a little higher than the  $c_{\min}$  values for separate Cu(II), Ni(II), Co(II), and Zn(II) ions and lower than  $c_{\min}$  for Fe(III), Cd(II), and Hg(II) (Table 3). With consideration for the inequality

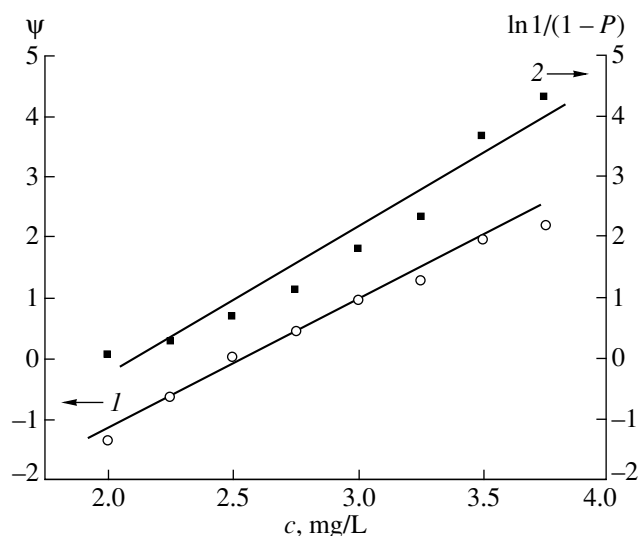
$$\sum_{\text{ion}} \frac{1}{c_{\min, \text{ion}}} = 1.59 \text{ L/mg} \gg \frac{1}{c_{\min, \text{total}}} = 0.25 \text{ L/mg}, \quad (7)$$

**Table 4.** Results of observation and calculated  $c_{\min}$  values ( $n = 50$ )

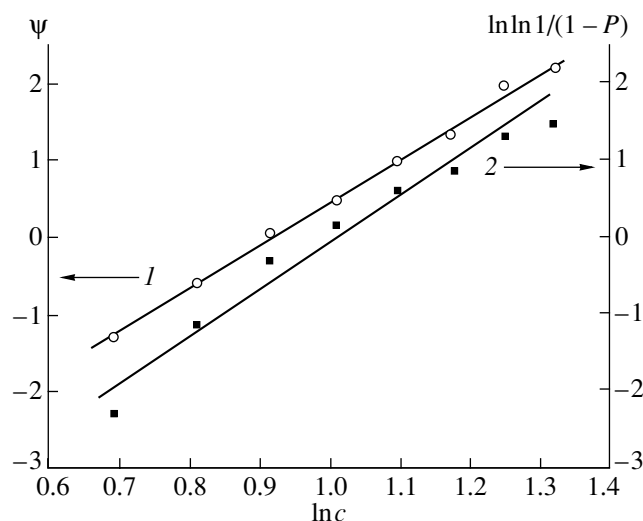
Parameter	$c_{\text{set}} = 6.0$ mg/L (without preconcentration)			$c_{\text{set}} = 6.0 \times 10^{-3}$ mg/L (with preconcentration)		
	Observer's answers, mg/L	10	7.5	5	$10 \times 10^{-3}$	$7.5 \times 10^{-3}$
Number of determinations	0	37	13	1	35	14
$s_c$		1.4			$1.5 \times 10^{-3}$	
$c_{\min}$		4.2			$4.5 \times 10^{-3}$	

**Table 5.** Detection frequencies of total metals

Procedure without preconcentration				Procedure with preconcentration			
$c_k$ (mg/L)	$N_k$	$n_k$	$P(c_k)$	$c_k \times 10^{-3}$ (mg/L)	$N_k$	$n_k$	$P(c_k)$
2.00	316	30	0.095	3.70	300	34	0.113
2.25	300	82	0.273	3.80	280	78	0.279
2.50	316	163	0.516	3.90	300	132	0.440
2.75	300	205	0.683	4.00	280	182	0.649
3.00	316	265	0.839	4.10	300	240	0.800
3.25	300	271	0.903	4.20	280	249	0.889
3.50	316	308	0.975	4.30	300	275	0.917
3.75	300	296	0.987				



**Fig. 2.** Test for the agreement between the detection frequencies of total metals found by the procedure without preconcentration and (1) the normal and (2) exponential distributions.



**Fig. 3.** Test for the agreement between the detection frequencies of total metals determined by the procedure without preconcentration and (1) the lognormal and (2) Weibull distributions.

we can state that metal ions exhibit a synergetic effect in the test determination of their sum.

The shape of the distribution function for the detection frequencies of total metals with and without preconcentration in the unreliable reaction region (Table 3) was selected from experimental results for seven or eight concentrations. For each concentration, 300 to 305 observations were made (Table 5). Some relationships used for the graphical testing of hypotheses about the agreement between the empirical and theoretical distributions are shown in Figs. 2 and 3. The regression coefficients in the relationships obtained (Table 6) indicate that the empirical distributions of detection frequencies for total metals are most close to the lognormal distribution.

Somewhat different conclusions were reached based on statistical goodness-of-fit tests (Table 6). The Weibull law best describes empirical detection frequencies for both measurement modes. The following distribution parameters were obtained:  $a = 3.57 \times 10^{-3}$  mg/L,  $b = 0.43 \times 10^{-3}$  mg/L, and  $k = 1.81$  with preconcentration and  $a = 1.71$  mg/L,  $b = 0.95$  mg/L, and  $k = 1.96$  without preconcentration. Location parameter  $a$  denotes the lower boundary of the unreliable reaction region, and scale parameter  $b$  characterizes its width. The values of shape parameter  $k$  are significantly higher than 1, which indicates that the probability density function  $P(c)$  is a bell-shaped curve, slightly different from the normal distribution curve. Based on these results, we could independently and reliably estimate the width of the unreliable reaction region: the intervals

**Table 6.** Test for the agreement between the empirical distribution of detection frequencies of total metal ions and theoretical distributions

Theoretical distribution	Procedure without preconcentration						Procedure with preconcentration					
	$R$	$\lambda_{\text{exp}}$	$\chi_{\text{exp}}^2$ *	$\tilde{A}$	$\gamma_2$	$c_1$ (mg/L)	$R$	$\lambda_{\text{exp}}$	$\chi_{\text{exp}}^2$ **	$\tilde{A}$	$\gamma_2$	$c_1 \times 10^3$ (mg/L)
Normal	0.994	0.20	0.28	-0.4	-1.6	3.44	0.990	0.10	0.59	-1.1	-0.7	4.36
Lognormal	0.996	0.07	0.088	-0.6	-0.7	3.36	0.993	0.08	0.43	-1.0	-0.6	4.31
Weibull	0.983	0.06	0.086	-1.2	-0.8	3.36	0.985	0.07	0.16	-0.1	-1.1	4.35
Exponential	0.975	0.25	0.81	0.09	-1.1	3.50	0.988	0.27	1.73	-0.6	-1.4	4.55
Poisson	-	0.13	0.37	-0.5	-0.2	3.40	-	0.62	34.0	-0.4	-0.5	5.0

Note:  $R$  regression coefficient for the corresponding linearized relationship (Table 2).

$$*\chi_f^2 = 6^{(\alpha=5\%)} = 11.1.$$

$$**\chi_f^2 = 5^{(\alpha=5\%)} = 9.49.$$

**Table 7.** Determination of total metals in water samples by atomic absorption spectrometry and test methods ( $n = 3$ ;  $P = 0.95$ )

Sample	Atomic absorption (mg/L)	Test method	
		mg/L	sample preparation
Mirgorodskaya mineral water	$0.242 \pm 0.006$	$0.20 \pm 0.15$	Without preconcentration
Berezovskaya mineral water	$0.0059 \pm 0.0005$	<0.20	Same
Spring water	$0.0124 \pm 0.0005$	<0.20	"
Severskii Donets River water	$0.382 \pm 0.009$	$0.35 \pm 0.15$	With preconcentration

$a-c_1$  were found to be  $(3.6-4.4) \times 10^{-3}$  and 1.7–3.4 mg/L for the procedures with and without preconcentration, respectively.

To validate the test procedure with the use of RIB, real samples were analyzed by independent methods. The results of determining total Co, Cu, Fe, Ni, and Zn by the test method and atomic absorption spectrometry after the 100-fold preconcentration of water samples by evaporation are compared in Table 7. No evaporation was used for the test analysis of water from the Severkii Donets River. The results of analyses coincided, and systematic errors were insignificant.

The relative error of semiquantitative visual analysis using a standard color scale with metal concentrations increasing in geometric progression with a common ratio of 2 ( $c_{n+1} = 2c_n$ ) varies from 33 to 100% [17].

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