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# Estimation of Detection Limits of Test Methods for Water Analysis

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It is suggested to specify the test methods based on visual evaluation of a useful signal by the probability distribution law and its parameters related to the detection limits. When solving a definite analytical problem, the known distribution parameters allow to calculate a detection probability of any concentration of the determinand, and vice versa, a concentration value corresponding to a preselected probability. Laws of probability distribution, their parameters and determinands detection limits in surface waters—by indicator test papers, colour reactions on a carrier, in solution and in a thin-layer adsorbent—have been investigated by the maximum likelihood and  $\chi^2$  minimum methods. The normal, lognormal, exponential, and Weibull distributions are corresponding to the tested types of methods. Such approach allowed an advantageous implementation of rapid assays for detection and quantitative determination of Na, K, Rb, Cs, Li, Cu(II),  $\text{NO}_2^-$ , 3,4-DCA, propanil, sevin, DDT, etc., in surface waters.

**KEY WORDS:** Water analysis, test methods, detection limits.

## INTRODUCTION

Analytical practice adopts rapid assays with the help of chromogenic reagent papers, colorimetric tubes with fixed ligands, reactions on carriers and printed reagent devices. Such assays are popular due to their simplicity and efficiency in monitoring of environment, chemical raw materials, in medicine and biology. Efficient application of these methods demands preliminary study of the probability distribution law related to a detection limit, and of the distribution parameters. We have investigated and applied such an approach for evaluation of detection limits of some normative substances in the surface waters, and this allowed to utilize a complete analytical potential of the methods.

### Selection of the detection limit criterion

Dispersion of the assay reaction observation data is caused by fluctuations in the assay conditions (temperature, reagents grade, purity of glassware, properties of carrier, etc.) within limits acceptable for the assay algorithm, and also by personal characteristics of operators and observers. The Kaiser detection limit, adopted by IUPAC<sup>1,2</sup> for visual colour equalization of the tested and the standard samples is unacceptable due to difficulties of numerical evaluation of a blank signal and its variance. The Kaiser criterion is based on an assumption of normal distribution of results, though there are no sufficient theoretical or experimental data on forms of the distribution near a detection limit. The same difficulties are characteristic for a "determination limit":

$$X = X_{\text{blank}} + K[S_{\text{blank}}]$$

The recommended empirical factor  $K=10$  is too coarse signal characteristics, determined by the test method. The American Society for Testing Materials (ASTM) employs "limit of detection criterion"<sup>5</sup> where the useful signal differs from the blank experiment signal only by a standard deviation value, i.e.,  $K=1$ , and the error probability one in three is acceptable. For some analytical problems even such indefinite information is sufficient, though this criterion is also based

on arbitrary selection of the factor  $K$  value. In our opinion, value of  $K$  must be determined in the framework of a specific problem, and not by arbitrary selection. The probability of a substance detection as a function of concentration in a sample is the most important characteristic of the test method. Knowledge of the law of probability distribution and of its parameters allows to calculate detection probability of any concentration ( $C$ ) of the substance, and v.v., to calculate  $C$  value corresponding to a given detection probability, as determined by a specific analytical problem.

### Experimental

Detection limits of assay methods have been investigated, as presented in Table 1. Algorithms of the methods are described in references given in the table. Procedures for detection of lithium, sodium, rubidium, and caesium are the same as described earlier for potassium.<sup>6</sup>

Statistical data were collected by visual indications of analytical responses in the assays. Detection limits were evaluated by a group of 10–15 independent observers. The uncertain reaction boundaries within which some samples give positive, and some negative results<sup>11</sup> were preliminary roughly estimated by small number of observations. Then, a large number  $N_i$  of observations (from 200 to 2000) were performed on several concentrations  $C_1, C_2, \dots, C_i, \dots, C_m$  from this domain and all positive results  $n_i$  were registered. The narrower the uncertain reaction domain, the more accurate are determined concentrations data based on the test. Probability of a determinand detection by the test method for a randomly selected observer equals the value of probability distribution function at the point corresponding to the determined concentration in the sample. A functional relationship of the positive result of observation  $P(C_i)$  and of concentration was approximately evaluated by experimental frequencies of detection  $\hat{P}(C_i)$ :

$$P(C_i) \approx \hat{P}(C_i) = n_i/N_i.$$

In Table 2 are given, as an example, experimental detection frequencies  $\hat{P}$  of Li with potassium croconate on a fluoroplastic plate.

Table 1 The probabilities distribution law evaluation results and test methods substances detection limits

Substance	Reagent, applications	Unreliable domain mg/l	Total number of observ.	Distribution type	Detection limit mg/l		
					at $P=0.95$	at $P=0.99$	at $P=0.99$
<i>l</i>	2	3	4	5	6	7	7
Li	$K_2C_2O_5$ on fluoroplastic	51-71	1600	normal	71		75
Na	$K_2C_2O_5$ on fluoroplastic	3-9	2000	normal	8.9		10
K	$Na_2C_2O_5$ on fluoroplastic <sup>6</sup>	1-6	2000	lognormal	6		8
Rb	$Na_2C_2O_5$ on fluoroplastic	2-21	1400	lognormal	21		35
Cs	$Na_2C_2O_5$ on fluoroplastic	4-89	3500	Weibull	88.5		123
Na	$K_2C_2O_5$ on porcelain <sup>7</sup>	18-26	2768	exponential	26		30
K	$Na_2C_2O_5$ on porcelain <sup>8</sup>	14-18	402	exponential	18		20
Cu(II)	РИБ ФММОПФ-6-Ц	0.0005-0.0025	140	Weibull	0.003		0.004
$NO_2^-$	4-DAB	0.9-2.5	907	normal	2.8		3.0
Propanil	2-naphthol-3,6-sulphoacid on alumina <sup>9,10</sup>	0.06-0.11	183	lognormal	0.11		0.13
Propamil	2-naphthol-3,6-disulfonic acid on silufol <sup>9,10</sup>	0.01-0.02	150	lognormal	0.02		0.022
3,4-dichloro aniline	2-naphthol-3,6-disulfonic acid on alumina <sup>9,10</sup>	0.03-0.15	514	lognormal	0.12		0.17
Sevin	4-amino-antipyrine on silufol <sup>9,10</sup>	0.012-0.020	750	lognormal	0.022		0.025
Sevin	4-aminoantipyrine on alumina <sup>9,10</sup>	0.007-0.014	188	lognormal	0.015		0.017
DDT	$AgNO_3$ on silufol <sup>9,10</sup>	0.001-0.01	768	lognormal	0.006		0.007

**Table 2** Frequencies of Lithium detection with potassium croconate and auxiliary functions for graphical control of the probabilities distribution type

NO	CLi mg/l	$N_i$	$n_i$	$\hat{P}$	$\log_e C_i$	$\log_e \left( \frac{1}{1-P} \right)$	$\log_e \log_e \left( \frac{1}{1-P} \right)$	$\psi(\hat{P})$	$P(C)$
1	55	228	32	0.1404	4.007	0.151	-1.889	-1.08	0.167
2	57.5	228	68	0.2982	4.052	0.354	-1.038	-0.52	0.291
3	60	228	108	0.4737	4.094	0.642	-0.443	-0.07	0.447
4	62.5	226	147	0.6504	4.135	1.051	0.050	0.39	0.602
5	65	228	188	0.8246	4.174	1.741	0.554	0.93	0.759
6	67.5	221	200	0.9050	4.212	2.354	0.856	1.31	0.868
7	70	134	127	0.9478	4.249	2.953	1.083	1.63	0.937
8	72.5	68	65	0.9559	4.284	3.121	1.138	1.75	0.974

## RESULTS AND DISCUSSIONS

The empirical frequency  $\hat{P}(C)$  obtained from a large number of observations gives sufficiently exact evaluation of  $P(C)$  probability. Influence of the number of tests on exactness of the probability evaluation<sup>12</sup> can be determined by the value of standard deviation of  $\hat{P}(C)$  evaluation:

$$\sigma(\hat{P}(C)) = \sqrt{P(C)[1-P(C)]/N}.$$

Let us evaluate, e.g., value for  $P=0.14$  (first line of Table 2):

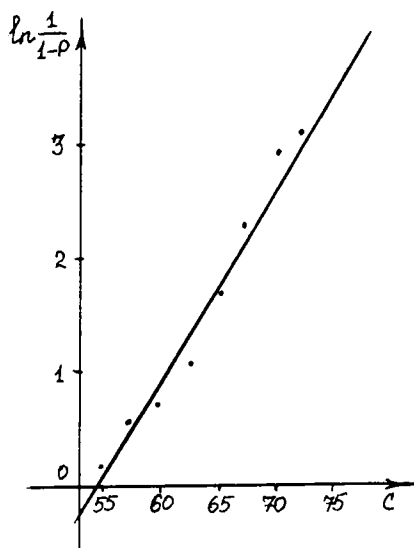
$$\sigma(\hat{P}(55)) = \sqrt{\frac{0.14(1-0.14)}{228}} = 0.023.$$

The evaluation of  $P(C)$  is sufficiently exact (2%). If  $\sigma(P(C))$  value is too large, it can be lowered by increment of the number of experiments at separate points. The model matching with an experiment was evaluated by matching rectified graphs of the concentration-frequency functions relation for  $P(x)$  families most widely used in practice, i.e., normal, lognormal, exponential and

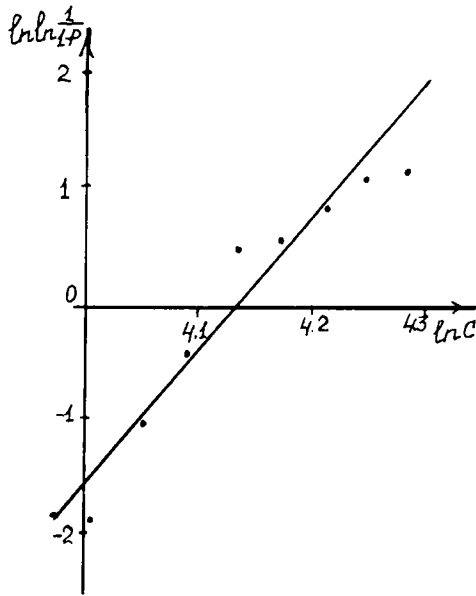
Weibull distributions. Graphical evaluation of the distribution parameters is sufficiently exact for majority of practical problems. If required, such methods can be used for initial approximation to more strict approaches on computers, such as the maximum likelihood and  $\chi^2$  minimum methods (where computers are necessary).<sup>13</sup>

Table 2 exemplifies estimation of auxiliary functions for graphical control of the type of Li detection probability distribution. Li has been detected by colour reaction with potassium croconate on a fluoroplastic plate. The control (Figures 1–3) demonstrated the best fit of experimental points to the normal distribution. From Figure 1, presenting the plot of normal distribution, it is easy to find parameters of function  $\zeta$  and  $1/\sigma$  presented by intercept with abscissa axis and by tangent, and equal to 60.8 and 0.17, correspondingly.

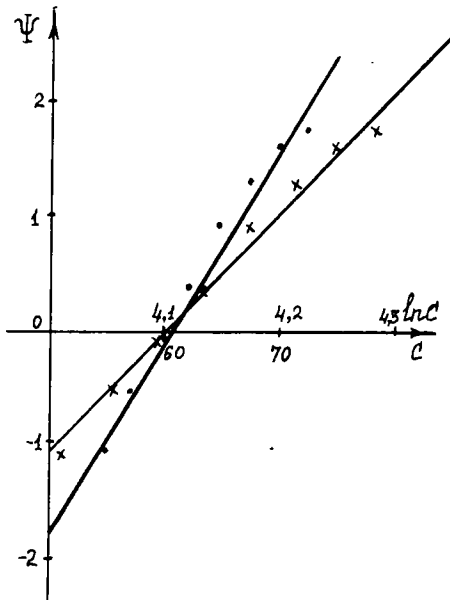
Such plots and calculations have been performed also for other substances and methods. The results, summarized in Table 1, indicate that even to the methods of the same type not only the normal distribution can be attributable. So, when elements of 1a subgroup were detected by the same rapid assay—with croconic



**Figure 1** Graphical verification of the exponential distribution agreement with experimental frequencies of lithium detection.



**Figure 2** Graphical verification of the Weibull distribution agreement with experimental frequencies of lithium detection.



**Figure 3** Graphical verification of the normal (·) and the lognormal (×) distributions agreement with experimental frequencies of lithium detection.



acid—the normal distribution of experimental points was obtained only for Li and Na. For K and Rb the points assembly is approaching the straight line in the case of lognormal distribution, and for Cs this is true for the Weibull distribution. The same type of distribution was obtained in a rapid assay for Cu(II), depending on Cu(II) colour reaction with a chromogenic reagent co-valently fixed to cellulose. The exponential distribution proved the best for Na and K detection methods with croconic acid on porcelain base. The distribution parameters were evaluated by the maximum likelihood method through differences between models and proved on the whole to be small. All investigated methods of substances detection in a thin layer of sorbent<sup>9,10</sup> exhibited the best fit to the lognormal distribution (Table 1). In this case the problem of a distribution type selection was solved by use of data for various substances. As the test of goodness of fit,  $\chi^2$  criterion was used:

$$\chi^2 = \sum_{k=1}^K \left\{ \sum_{i=1}^{M_k} \frac{[n_i - N_i P(C)]^2}{N_i P(C_i) [1 - P(C_i)]} \right\}$$

with the degree of freedom number

$$A = \sum_{K=1}^K (m_k - 2) = \sum_{k=1}^K m_k - 2K.$$

Here  $k$  = determinand number,  $K$  = number of all determinands,  $N_i$  = number of experiments for  $C_i$  by a corresponding method,  $n_i$  = number of positive results,  $m_k$  = number of concentrations investigated by  $K$ th method,  $P(C_i)$  = probability computed by assessed distribution function parameters. After exclusion of far scattered points,  $\chi^2 = 35.87$  at  $f = 21$  was obtained, which is less than  $\chi^2(0.01) = 38.93$  for the significance level 0.01. For assay methods based on a treatment of thin-layer chromatograms with colouring reagents, the experimental data as a rule correspond to the lognormal distribution. The found values of distribution function parameters allow to calculate probabilities of detection of tested determinand concentrations, and vice versa, concentrations corresponding to a prescribed  $P$  probability can be found by  $P(C)$  formula.<sup>12</sup> The values of  $P(C)$  calculated, e.g., for investigated Li concentrations, are given in the last column of Table 2. Concentrations  $P = 0.95$  or  $0.99$  (last columns of Table 1) can be accepted as detection limits.

The obtained characteristics of test methods allowed to use them as indicators, signalling of overstepping of maximum allowable concentration (MAC) with a preselected probability, and also to use them for quantitative evaluations. Rapid indicator tests with detection limits close to MAC are the most convenient ones. In a rapid assay, e.g., of  $\text{NO}_2^-$  (Table 1) the concentration corresponding to  $P=0.95$  is 2.8 mg/l, and MAC for water bodies with household water use is 2 mg/l. If the reaction of  $\text{NO}_2^-$  detection with 4-DBA is positive, then one can claim with 95% probability that  $\text{NO}_2^-$

**Table 3** Comparative results of  $\text{NO}_2^-$  detection in model solutions, natural waters and effluents by the visual rapid test with 4-DBA (a) and the Griess reagent (b) ( $n=3$ )

Sample	Impurity ions mg/l	Detection method	Introduced mg/l	Detected $S_r$ mg/l	
Model solution	$\text{NH}_4^+ = 5$ $\text{NO}_3^- = 10$	a	1.7	2.0	0.3
		b	1.7	1.8	0.05
		a	2.7	2.4	0.1
		b	2.7	2.6	0.05
River water I	$\text{Cl}^- = 91$ $\text{HCO}_3^- = 140$ ; $\text{NO}_3^- = 0.02$ $\text{NH}_4^+ = 2.3$ ; Oil prod. = 0.5	a	without	2.1	0.2
		b	intr'on	1.6	0.06
		a	3.4	3.3	0.1
		b	3.4	3.7	0.07
		a	5.0	4.7	0.2
		b	5.0	5.1	0.01
River water II	$\text{Cl}^- = 49$ ; $\text{NH}_4^+ = 1.8$ $\text{NO}_3^- = 14.8$ ; Oil prod. = 0.29	a	without	2.8	0.1
		b	intr'on	2.9	0.03
		a	3.4	3.1	0.1
		b	3.4	3.2	0.03
Effluents of nitrogenous fertilizers plants	$\text{NH}_4^+ = 20$ $\text{P}_2\text{O}_5 = 15$ $\text{SO}_4^{2-} = 100$ $(\text{NH}_2)\text{CO} = 50$ $\text{NO}_3^- = 60$	a	without	2.4	0.1
		b	intr'on	2.6	0.05
		a	3.6	3.3	0.1
		b	3.6	3.8	0.03
		a	6.0	5.8	0.2
		b	6.0	6.1	0.02

concentration is above MAC. If colouring is absent, then, with a risk of mistake 5 in 100, one can claim that  $\text{NO}_2^-$  concentration is less than 1 mg/l. Results of  $\text{NO}_2^-$  quantitative determination in waters by the test method are compared in Table 3 with that of the photometric method with the Griess reagent. The results are without systematic error and differ only by  $S_r$  value.

The test method of Cu(II) determination with the reactive paper РИБ ФММОПФ-6-Ц<sup>14</sup> proved to be most accurate for analysis of its concentration in waters.

## CONCLUSIONS

It is proposed to evaluate detection limits of substances in surface waters with the help of test methods by preliminary study of the probability distribution, by graphical procedures and by the maximum likelihood and  $\chi^2$  minimum. Colour reactions were investigated on indicator test papers, on carriers, on thin-layer adsorbents and in solutions. It has been found that various types of distribution—normal, lognormal, exponential, and the Weibull ones—can correspond not only to different types of methods, but also to methods of the same type. The offered approach allows maximal implementation of analytical potentials of the test methods.

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