

# Limit of detection in spectrochemical analysis for a background intensity varying with wavelength

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Received 20 July 1972

The value of background blackening in a point corresponding to the wavelength of signal as well as the standard deviation for the variation of spectral background in the proximity of this wavelength was determined by the method of regression analysis. The described procedure enables to determine the limit of detection even if the background intensity in the proximity of the investigated spectral line varies with wavelength.

At present, the limit of detection of chemical analytical methods may be defined unambiguously by means of mathematical statistics. *Kaiser* [1] was the first to apply this procedure to the calculation of the limit of detection in emission spectrochemical analysis with photographic record. This problem was treated also in further papers [2–6].

The spectrochemical determination of elements is limited by the fact that a decrease in the content of trace elements may result in a state in which the spectral lines cannot be distinguished any more from the spectral background. The limit of detection may be defined when the intensity difference between a line and an average value of background is equal to the threefold standard deviation of the background variation. The corresponding concentration of substance may be calculated by the extrapolation of an analytical curve which refers to the concentration range in a reliably measurable region [3].

*Kaiser* based the determination of the limit of detection on the assumption that the signal under consideration occurs on the background of a continuous spectrum without structure, the intensity of which is equal before and behind the spectral line and does not change with the wavelength. In this case the determination of the intensity of background at the wavelength of signal is not very difficult. The determination of the value of background and its standard deviation is much more complicated if the spectral line appears on the background which has a structure caused by molecular bands or some traces of impurities in electrodes, admixtures or in the air. The problem of determining the limit of detection if the investigated line occurs on such background was treated by *Boumans* and *Maessen* [7, 8].

As to the evaluation of the limit of detection there are no references in literature how to determine the value of varying background in the proximity of signal if the background intensity is different on the both sides of the spectral line, *i.e.* if it depends on wavelength which relatively often appears in practice. This paper is therefore dedicated to this problem.

## Experimental

The background record shows a certain variation of values the mean of which may be estimated graphically but the value of the background intensity thus obtained at the wavelength of signal is not sufficiently reliable for the determination of the limit of detection.

In order to improve the precision in the estimation of background variation at the wavelength of investigated spectral line, it was necessary to determine the value of background intensity in a point corresponding to the wavelength of signal as well as the standard deviation for the variation of its values in the proximity of this wavelength. For this purpose a more precise method of calculation had to be used. For the solution of this problem we used the records obtained by photometric measurement of the photographic plates with the records of the spectra of artificially prepared model sample.

The model sample should be chosen so that the investigated element would have a spectrum with a convenient spectral line but no interfering lines would occur in the proximity of this line. We did not choose any element which is usually present in laboratory atmosphere like Si, Mg, Ca, Fe because the contamination might impair the results. Another condition of this selection was that the chosen spectral line should occur on a continuous spectrum which did not show any measurable systematic structure. Otherwise, the evaluation would be very complicated. Thallium fulfils these conditions. We used its spectral line with the wavelength of 5350.46 Å.

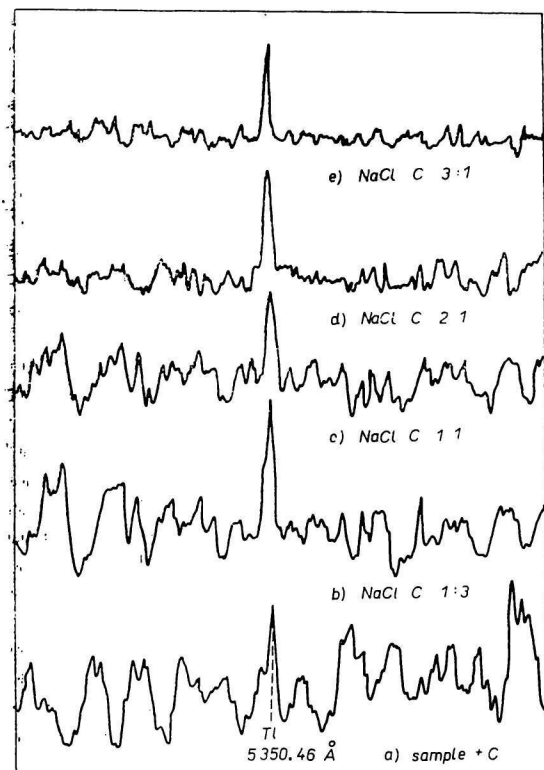


Fig. 1. Effect of NaCl on the suppression of the structure of background.

Tl content in weight %.  
 a) sample + C; b) NaCl : C (1 3); c) NaCl : C (1 1); d) NaCl : C (2 1); e) NaCl : C (3 : 1).

The model samples with different mass ratios were so prepared that a solution with a certain content of  $Tl_2CO_3$  was added into the mixture of NaCl and C with mass ratio 1 : 3. Sodium chloride was chosen because it had a very good effect on the suppression of background and the variation of its values. The relative proportion of NaCl in the mixture was found out experimentally. The effect of NaCl on the background in the proximity of investigated spectral line can be seen in Fig. 1.

The composition of samples was in the range from  $5 \times 10^{-7}$  to  $10^{-4}$  weight % of thallium.

The spectra were excited in an a.c. arc. A generator DG-2 with 4 A intensity was used as a source.

Graphite electrodes SU-102 and graphite rod material Electrocarbon, Topolčany, was applied. The carrier electrodes were shaped into a form of cavity electrode. The inner diameter of the cavity, depth, and width of walls were 2 mm, 6 mm, and 0.5 mm, respectively. A rod of 4-mm diameter SU-204 with conic end served as a counter-electrode. The electrode gap was adjusted to 2 mm at the beginning of exposure and was not altered during burning. The exposure time was 60 seconds.

A three-prism glass spectrograph ISP-51, with a 304 mm collimator and a camera of 270 mm focal length was used.

The slit was illuminated by means of a three-lens system with intermediate imaging, the height of the intermediate diaphragm and the slit width being 2.0 mm and 0.005 mm, respectively.

The spectra were photographed on superpanchromatic plates ORWO NP-22 which were almost equally sensitive for the whole region of the visible spectrum. These plates possess a sufficiently high value of  $\gamma$  with a very good response to radiation.

The exposed plates were developed in a metol-hydroquinone developer DF-8 diluted in the ratio 1 : 2 for two minutes at 19°C.

The records of spectra were obtained by microphotometric evaluation with a microphotometer G-II (Zeiss, Jena) equipped with a motor for the shift of plate. The selenium element of microphotometer was connected to an EZ-4 recorder with maximum sensitivity of  $0.5 \mu V/mm$ . One millimeter on the spectral plate corresponded to 230 mm of recording paper. The records thus obtained served as a basis for the calculation of the value of background in a point corresponding to the wavelength of signal as well as for the calculation of the standard deviation of the background variation in its proximity.

## Results and discussion

The problem was solved by the method of regression analysis which helped to estimate better the relationship between two or several variables; the numerical values of variables  $y$  were obtained from the measured data.

In measurements,  $m$  pairs of the values  $(x_i, y_i)$  were found out. The dependence of  $y'$  on  $x$  may be expressed in the investigated, relatively narrow region with sufficiently high precision by the linear relationship  $y' = a + bx$ .

The constants  $a$  and  $b$  of this function were determined by the method of least squares. The calculations were performed with a computer using a programme developed specially for this purpose.

The input data were found out as follows.

The record obtained under mentioned conditions was evaluated in such way that in the point  $x = 0$  the spot of the occurrence of signal was marked. The height of this signal was measured (in mm) and thus the value of  $y_{x=0}$  was obtained. Then, starting

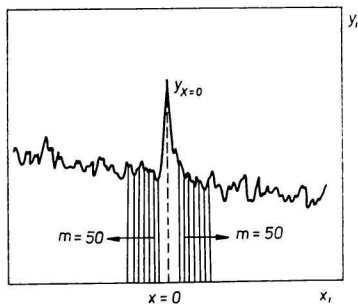


Fig. 2. Evaluation of a record.

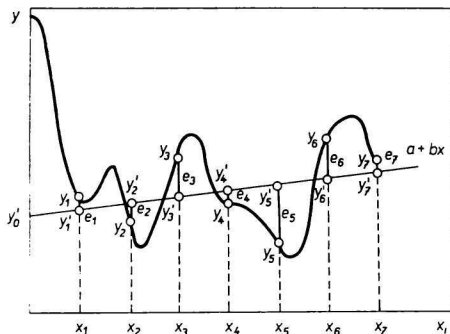


Fig. 3. Enlarged section of the record of Fig. 2. Determination of the values needed for the calculation of deviations.

from the point  $x = 0$  the heights of the signals of background  $y_i$  were measured in regular distances of 2 mm each on the left and on the right from this point which represented 50 values on either side, in total 100 values on 5 parallel arcings for each concentration (Fig. 2).

On the basis of these data the course of regression curve fixed by the constants  $a$  and  $b$  as well as the respective values of  $y'$  were found out by means of a computer for all the values of  $x_i$  employed.

The used recording photometer gives the records in  $1 - T_x$  ( $T_x$  being transparency). In the narrow range of values involved in our measurements the above function may be assumed as a linear function of intensity with sufficient accuracy. With respect to the relative character of intensities used in spectrochemical practice [9] the above function.

The values proportional to it are denoted for the purpose of regression analysis as follows: experimental values  $y$ , calculated values  $y'$ . The standard deviation of the variation of background  $s_V$  necessary for the determination of the limit of detection was found as follows: In each point measured ( $i$ ) (50 values on the right side and 50

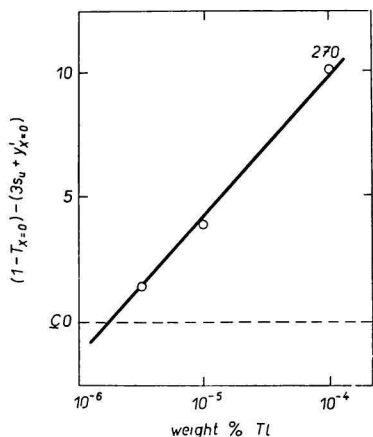


Fig. 4. Calibration curve for the determination of the limit of detection.

values on the left side from the line) the difference between the experimental ( $y_i$ ) and calculated value ( $y'_i$ ) was determined. This difference gives the corresponding deviation (écart)  $e_i$ :

$$e_i = y_i - y'_i = y_i - a - bx_i.$$

Owing to a great number of measurements ( $m = 100$ ) the estimation of standard deviation is with a high degree of probability given by the expression

$$s_U = \pm \left( \frac{\sum_{i=1}^m e_i^2}{m} \right)$$

An enlarged section of the record (Fig. 2) presented in Fig. 3 shows how the values necessary for the calculation of deviations were established.

Table 1

<i>I</i>		<i>I</i>		<i>I</i>		<i>I</i>		<i>I</i>	
$c$ [weight %]	<i>N</i>	$y'_{x=0}$	$3s_U$	$3s_U + y'_{x=0}$	$1 - T_{x=0}$	$(1 - T_{x=0}) -$ $-(3s_U + y'_{x=0})$			$\bar{X}$
0	1	7.33	0.35	1.05	8.38	7.2	-1.18		
	2	6.42	0.39	1.17	7.59	6.8	-0.79		
	3	7.51	0.42	1.26	8.77	7.9	-0.87		
	4	6.38	0.35	1.05	7.43	6.8	-0.63		
	5	7.16	0.34	1.02	8.18	8.0	-0.18		-0.73
$5 \cdot 10^{-7}$	1	6.17	0.42	1.26	7.43	6.9	-0.53		
	2	6.63	0.36	1.08	7.71	7.4	-0.31		
	3	7.72	0.35	1.05	8.77	8.4	-0.37		
	4	7.65	0.34	1.02	8.67	8.0	-0.67		
	5	6.39	0.45	1.35	7.74	7.3	-0.44		-0.46
$10^{-6}$	1	7.03	0.38	1.14	8.17	7.9	-0.27		
	2	7.67	0.35	1.05	8.72	8.7	-0.02		
	3	6.39	0.43	1.29	7.68	7.4	-0.28		
	4	4.78	0.66	1.98	6.76	6.9	0.14		
	5	7.35	0.36	1.08	8.43	8.1	0.33		-0.02
$5 \times 10^{-6}$	1	6.65	0.38	1.14	7.79	8.9	1.11		
	2	8.17	0.36	1.08	9.25	11.0	1.75		
	3	7.89	0.43	1.29	9.18	10.7	1.52		
	4	8.66	0.39	1.17	9.83	11.0	1.17		
	5	8.20	0.38	1.14	9.34	10.9	1.56		1.42
$10^{-5}$	1	8.31	0.31	0.93	9.24	12.6	3.36		
	2	7.59	0.33	0.99	8.58	12.3	3.72		
	3	6.11	0.36	1.08	7.19	11.1	3.91		
	4	8.52	0.41	1.23	9.75	13.5	3.75		
	5	7.44	0.38	1.14	8.58	12.7	4.12		3.77
$10^{-4}$	1	9.55	0.38	1.14	10.69	19.6	8.91		
	2	8.43	0.33	0.99	9.42	19.3	8.91		
	3	7.70	0.39	1.17	8.87	19.5	10.63		
	4	8.90	0.36	1.08	9.98	20.4	10.42		
	5	8.16	0.45	1.35	9.51	20.6	11.09		9.99

Using the above experimental conditions and the described method of regression analysis we obtained the results given in Table 1.

The mass ratio of samples in column 1 is expressed in weight % of thallium. The mass ratio for  $c = 0$  corresponds virtually to a blank test checking the purity of chemicals, carbon electrodes, and atmosphere of discharge. The record of the blank test did not show any signal at the investigated wavelength, what meant that the carbon material used, chemicals, and laboratory atmosphere were free of thallium. Furthermore the repeated record of the spectra of all five parallel experiments confirmed that the continuous background on which the signal occurred was without any systematic structure and the continuous spectrum was affected only by a random variation of background. Column 2 gives the sequence of experiments. In column 3 the values of background  $y'_{c=0}$  at the point  $x = 0$  calculated by regression analysis are presented. The calculated values of the estimate of standard deviation  $s_U$  of the variation of background are in column 4; the threefolds of these standard deviations are in column 5. The values in column 6 have been calculated according to the condition [1-3] used for the definition of the limit of detection  $c = 3s_U + y'_{x=0}$ . Column 7 contains the values of signal  $1 - T_{x=0}$  at the wavelength of thallium (5350.46 Å) at the point  $x = 0$ . The values of the expression  $(1 - T_{x=0}) - (3s_U + y'_{x=0})$  in column 8 represent the difference between the value of signal and the threefold of the standard deviation of the variation of background. In column 9 the arithmetic means of the values in column 8 are given. The values denoted with minus sign (-) refer to lower values of signal than the value of  $3s_U + y'_{x=0}$ . Thus it means that the signal disappears on the varying background and cannot be detected on the record with required statistical reliability.

Using the above values we constructed an analytical curve. The values  $(1 - T_{x=0}) - (3s_U + y'_{x=0})$  are on the axis of ordinates while the percentage of thallium is on the axis of abscissas (Fig. 4).

Fig. 4 represents the analytical curve which is constructed by means of the values obtained by the method of regression analysis namely the values with positive sign (+) listed in Table 1. By extrapolating the curve to the point  $(1 - T_{x=0}) - (3s_U + y'_{x=0}) = 0$  the limit of detection  $c$  may be found [1-3]. The values below this limit are in Table 1 denoted with the sign (-) and are not significant since in these cases the signal disappears in the variations of background.

By this procedure the problem of the determination of the limit of detection in spectrochemical analysis was solved in a satisfactory way even if the intensity value of background in the proximity of signal changed with wavelength.

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Translated by R. Domanský