Determination of the effect of focal length of spectrograph camera on the limit of detection

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Received 20 July 1972

By the method of regression analysis the limit of spectrochemical detection of Tl was followed using a spectral instrument with varying focal length of camera. The experiments confirmed that with increasing focal length the possibility of detection improves only to a certain value.

The limit of detection obtained up to now in spectrochemical analysis does often not represent the optimal value. There are several papers devoted to the problem of the limit of detection in spectrochemical analysis. A critical survey of these papers dealing with the possibility of improving the limit of detection was given by *Laqua* [1].

The earlier studies were concerned with different enrichment procedures, chemical or physicochemical, leading to an improvement of the limit of detection. But these methods are laborious and require a longer time for the treatment of sample. The more recent studies are more concerned with an improvement in the parameters of exciting generators and spectral instruments as well as the properties of the radiation detectors used.

The relationship between the limit of detection and the instrument parameters was theoretically elaborated by *Kaiser* [2] who derived a general equation expressing the relation between the concentration of the analyzed substance and the parameters of spectral instrument. This study was later completed by *Laqua*, *Hagenah*, and *Waechter* [3] who took into consideration the properties of photographic plate as well. These authors carried out also the theoretical calculations according to which the limit of detection may improve by increasing the linear dispersion of instrument. Since the linear dispersion may also be increased by a greater focal length of camera, it is possible to obtain a lower limit of detection by using a spectral instrument with a camera of greater focal length [4].

In this study we performed some practical measurements which should demonstrate to what extent the focal length of camera affects the limit of detection.

Experimental

As stated before, the limit of detection depends on the focal length of used cameras. For our investigation we therefore chose an instrument with exchangeable cameras of different focal length and thus also different linear dispersion. Among the instruments available a three-prism glass spectrograph ISP-51 fulfilled the above requirements.

Table 1

Focal length F [mm]	Effective relative aperture	Linear dispersion for 5000 Å [Å mm^{-1}]
120	1 2.3	105
270	1 5.5	47
800	1 13.0	17.5

Table 2

Focal length F [mm]	120	270	800
Magnification	0.394	0.886	2.631

Table 3

Focal length of camera [mm]	Exposure time for one carbon [s]	Number of carbons	Intermediate diaphragm [mm]
120	60	1	0.8
270	60	1	2.0
800	60	10	5.0

It follows from the characteristics of this instrument that we confined in our investigation to the use of the visible region of spectrum.

The parameters of the used cameras are given in Table 1. The same collimator (focal length 304 mm) was used for all three cameras in order that only one parameter might be changed when investigating the dependence of the limit of detection.

Under these conditions the spectrograph shows an increasing magnification if cameras with shorter focal lengths are gradually exchanged for cameras with greater focal lengths (Table 2).

Other experimental data concerning the instrumental equipment and the preparation of samples and chemicals as well as the detection of radiation and recording of spectral lines were given in preceding paper [5].

The exposure time was so chosen that equal values of blackening were always obtained for the background of the spectrum taken with cameras with different focal lengths and these values varied in the range from 0.15 to 0.25 [3, 6]. When a camera with the focal length of 800 mm was used, we were not able to obtain such a density by the excitation of the filling of one electrode and for this reason ten electrodes were used for excitation. The exposure conditions chosen for individual cameras are given in Table 3.

According to the accepted criterion, the limit of detection is attained if the signal difference between the line and the mean value of background equals the triple value of the standard deviation of the background variation. In order to improve the precision of the estimation of background intensity at the wavelength of signal, it was necessary to use a more precise calculation method for the estimation of the background intensity in a point corresponding to a certain wavelength of signal as well as the standard deviation of its values in the vicinity of the investigated wavelength. To solve this problem we used the method of regression analysis described in paper [5].

Results and discussion

The spectra of samples with increasing content of thallium were taken by means of spectrographic cameras with different focal lengths. Under the above-described experimental conditions and using the described statistical method we obtained the values used for the construction of analytical curves (Fig. 1). The values of $(1 - T_{x=0}) - (3s_U + y'_{x=0})$ are plotted on the axis of ordinates and the percentage of Tl is on the axis of abscissas (Tl — transparency, s_U — standard deviation, y' — the values calculated by regression analysis [5]). In Fig. 1 there are three analytical curves constructed from the values obtained by photographing the spectra of Tl with three cameras of different focal lengths, *i.e.* $F = 120$, 270, and 800 mm.

By extrapolating the analytical curve to the point corresponding to $(1 - T_{x=0}) - (3s_U + y'_{x=0}) = 0$ it is possible to estimate the values of the limit of detection $\underset{\sim}{c}$. For individual cameras we found the limits of detection given in Table 4.

From Table 4 it is obvious that by using a camera with a greater focal length the limit of detection may be lowered by one decimal order. But it is necessary to point out that only the relative limit of detection may thus be improved [8] because, as stated before, the use of a camera with the focal length of 800 mm required a tenfold increase in exposure time to afford an equal value of background density as was obtained by means of other two cameras with focal length of 120 or 270 mm, respectively. It is evident that the limit of detection may thus be improved provided a sufficient amount of sample is available.

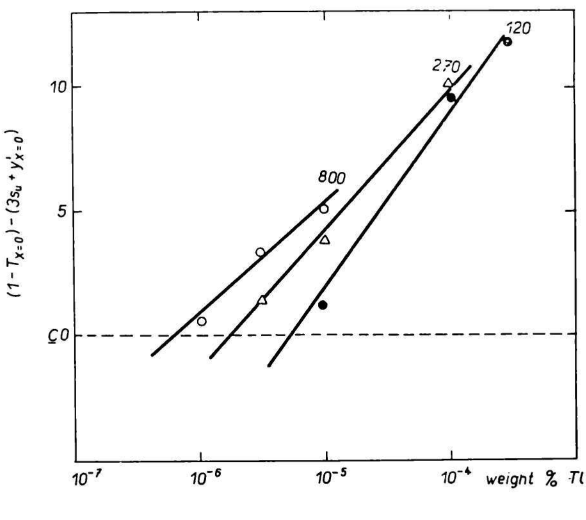

Fig. 1. Determination of the limit of Tl detection for cameras with different focal lengths ($F = 120$, 270, and 800 mm).

Table 4

F [mm]	120	270	800
$\underline{c}$ % Tl	$7.4 \times 10^{-}$	$2.3 \quad 10^{-6}$	0.8×10^{-6}

Fig. 2 shows the dependence of the limit of Tl detection on the focal length of cameras used. From this graph it can be seen that this value does not substantially change with the increasing focal length of camera provided a certain limiting value has been attained. Hence a further increase in focal length and thus also in linear dispersion of an instrument is not advantageous from the point of view of improving the limit of detection because this limit should be very close to the limiting value which would correspond to the use of a camera with infinite focal length. This is also indicated by the relationship between $\underline{c}$ (%) and the reciprocal value of the focal length of cameras (graph in Fig. 3) which shows that the limiting value $\underline{c} = 6.8 \times 10^{-7}$ % would have been attained for Tl if a camera with infinite focal length were used. That means that a further improvement in the limit of detection cannot be expected in this line, which is in good agreement with the paper of *Laqua, Hagenah,* and *Waechter* [3], and experimentally confirms their conclusions. These authors pointed out in their paper that not only the density of background decreases with focal length of camera (in our case this is confirmed by the fact that the exposure time had to be ten times increased for the camera with the focal length of 800 mm in order that an equal background density as with another two cameras might be obtained) but also the profile of line extends. As a matter of fact, the extension of the profile of line still results in decreasing of its blackening which improves neither the ratio of the intensity of line to the intensity of background variation nor the limit of detection. On the other hand, a trivial consequence ensues from the experimental results according to which the limit of detection increases to infinity for zero focal length, *i.e.* provided no spectrum appears at all.

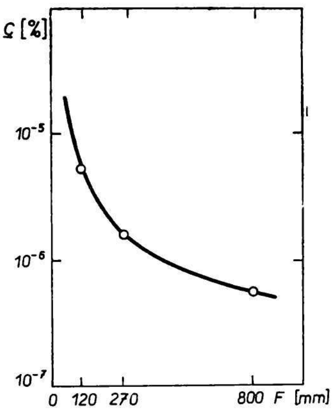

Fig. 2. Dependence of the limit of Tl detection on the focal length of camera.

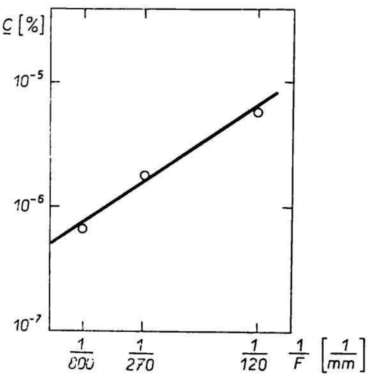

Fig. 3. Dependence of the limit of Tl detection on the reciprocal value of the focal length of camera.

It follows from the above facts that a certain compromise should be arrived at as regards the improvement in the limit of detection by changing the parameters of instrument responsible for linear dispersion. It must be taken into consideration whether a further expensive increase in the focal length of camera is balanced by a rather small improvement in the detection power of spectrochemical analysis.

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Translated by R. Domanský