RECTIFICATION OF PHOTOELECTRIC SPECTROMETER

By Kazimierz W. Ostrowski

II. Chair of Physics, Mining and Foundry Academy, Cracow

(Received September 4, 1959)

In the present paper formulas are derived for the tolerance of the disposition of the spectrometer camera exit-slit. Other formulas accounting for the curvature of the spectral line set a limit to the admissible height of the exit-slit. A practical rule for the rectification of the spectrometer is also given, the principal feature of which consists in the use of the Hartmann diaphragm. From higher order diffraction, the effect of neighbouring lines on the data recorded is assessed. Computation is adapted to the ИСП 22 spectrograph.

1. *Introduction*

In direct spectrometry, instead of the photographical plate a photoelectric detector (photomultiplier, photosensitive G.—M. counter) is introduced; the latter is displaced parallel to the focussing plane, within which displacement of the exit-slit occurs. During the measurement, the width of the slit is fixed so as to entirely comprise the spectral line. It is but rarely that a slit of lesser width than the line is used. In this case continuous recording is obtained with an instrument provided with an automatically recording milliampermeter wherein motion of the paper tape is coupled to that of the exit-slit with selsyns.

Although direct spectrometry has now been in industrial use for about 15 years, there exists as yet no systematic treatment of the problem of rectifying the camera with the photoelectric detector accounting for such factors as the power of separation, curvature of line, ambient temperature, pressure and atmospheric moisture content.

Some papers (Hanau and Wolfe 1948, Bryon and Nahstoll 1948, Naish 1951, 1952, Mostyn 1952, Soda 1953, Hagenmah 1954, and Carlsson 1954) give these problems passing consideration, and this but from an experimental standpoint. The present author intends to complete the foregoing papers by giving computations of the admissible tolerance in disposing the camera with the photoelectric detector. Such computations may be of interest, as similar problems have been dealt with in the case of grating spectrometers (Minkowski 1942, Rupert 1952, Fastie 1952 a, b.)

These authors considered i. a. the problem of chosing the curvatature radii of the entrance and exit-slits so as to eliminate aberration and astigmatism at all wavelengths when using a long slit.

2. *Assessement of tolerance in disposing exit-slit*

Assume a prismatic spectrometer to have been adjusted as spectrograph. By displacing a very narrow exit- slit parallel to the focussing plane, the profile of the line can be determined. The latter will be wider then natural for three reasons:

1. the plane of motion of the slit is at a distance g from the focussing plane, which moreover can differ for the various spectral regions,
2. the exit-slit generally subtends a non- zero angle, γ with the spectral line,
3. the spectral line possesses curvature of radius ϱ,

a. Assessment of admissible distance g between focussing plane and plane of motion of slit

Fig.1 shows the situation dealt with. R denotes the line-width measured at $g\neq 0$ assuming the width of the exit-slit, the intrinsic width of the line, and the width

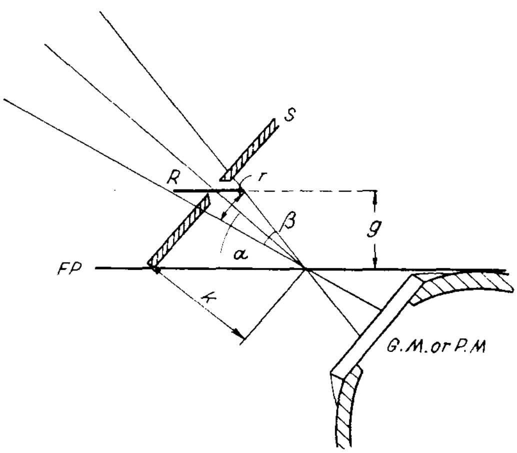

Fig. 1 Position of exit-slit S with respect to focussing plane FP

resulting from diffraction on the prims to be infinitesimally small. Introducing the notation g, α, β, R, r, k as in Fig. 1, we have, by elementary considerations:

$$R=\frac{r}{\sin\alpha}=\frac{k\sin\beta}{\sin\alpha}=\frac{g\sin\beta}{\sin^2\alpha}, \tag{1}$$

or

$$g=\frac{R\sin^2\alpha}{\sin\beta},$$

ACTA PHYSICA POLONICA Vol. XIX (1960) Fasc. 3

wherein sin β is a quantity identical with the relative aperture of the camera i. e. the ratio of the radius of the objective lense and its focal length. In the present considerations, values of g will be admitted for which $R = d$, with d denoting the width

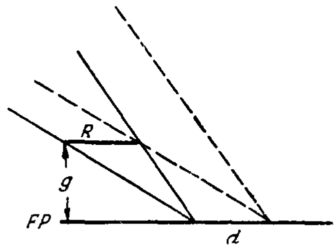

Fig. 2. Intrinsic width of line, d, and admissible width R as resulting from distance g of slit from focussing plane

of the spectral line (Fig. 2). If this width be assumed as the "instrument" line-width i. e. a half-width of the zero order diffraction maximum, then d is given by the well-known formula of the theory of optical instruments:

$$d = \frac{\lambda \sin \alpha}{\sin \beta}. \tag{2}$$

For the ИСП 22 spectrograph used by the present author in investigating photosensitive G.—M. counters (Ostrowski 1959), the following values of d and α hold (Prokofiev 1951):

Table 1

2000 Å	$d =$ 5.6 microns	$\alpha = 47°$
2570 Å	9.0 "	41°
5600 Å	23.0 "	37°

According to catalogue, the relative aperature of the objective lense in the ИСП 22 spectrograph is 0.05 for the spectral region of about 2570 Å. If these values are substituted in eq. (1), an admissible distance of about 0.1 mm is obtained. Let us compare this value and that assumed by Prokofiev for the same spectrograph when using photographic plates. In this case d is limited by the grain-size (ca. 20 microns). Prokofiev assumens the admissible distance of the plate and focussing plane to be 0.5 mm. It should be stressed that additional widening arises in the plane from dispersion of radiation in the emulsion, especially at greater wavelengths, for which gelatine exhibits lesser absorption. Resulting from non-perpendicular incidence, the long-wave side of the line will show greater diffluence, Hence adjustment of the photoelectric spectrometer requires a greater degree of accuracy; however, its separating power is higher, too. Similarly, temperature will affect the precision of adjustment to a greater degree (resulting in variations of the position of the line and in variations of g). On the other hand, such variations can be set right within a very short time by investigating the profile of the apprioprate line, whereas the photographic method makes it necessary to make test photographs. The value of g can be modified by introducing appropriataly cut props between the spectrometert and the camera; of a set of these are to hand, the camera can be set to the degree of accuracy required.

b. Assessment of maximum admissible angle between slit and line

Hitherto it has been assumed here that the height of the entrance-slit is so small that inclination in the exit-slit has no widening effect upon the of profile the line. Fig. 3 shows a spectral line L and profiling slit S. As admissible angle γ, the one will be here assumed at which the of edge of the slit is the diagonal of the spectral line. Then

$$\operatorname{tg} \gamma = \frac{d}{l}. \tag{3}$$

For $d = 10$ microns and $l = 10$ mm, the admissible angle is 0.05^0. Simultaneous setting of the slit to this degree of accuracy and continual control of the spectral line profile is a very tedious affair. The present author proposes to make this task easier as follows: an appropriate (narrow) line is subjected to separation with a Hartmann diaphragm placed just before the entrance-slit (Fig. 4). When profiling the

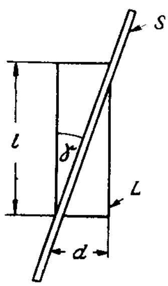

Fig. 3. Relative position of line and narrow exit-slit

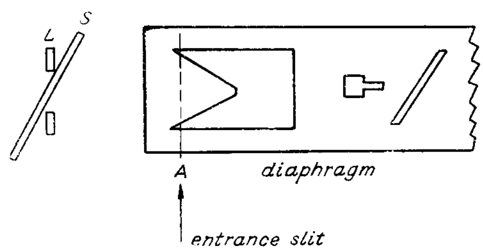

Fig. 4. Division of line for obtaining sufficiently small angle γ (method of blending of two maxima)

line two maxima are obtained; these can be made to coincide into one, presenting double intensity, if the camera is constructed so as to admit of rotating the slit through several degrees of the arc. The method proposed makes observation independent of the widening of the line profile arising from curvature. The higher the entrance-slit, the easier it becomes to attain parallel setting of the line and the exit-slit with an increasing degree of accuracy.

3. Limitation in height of entrance-slit relating to line curvature

The spectral line presents the shape of a parabola whose convexity is directed towards the short-wave end of the spectrum. This results form accounting for refrac-

ACTA PHYSICA POLONICA Vol. XIX (1960) Fasc. 3

tion outside the principal section of the prism. The radius of curvature of the line is given by the well- known Kaiser (1900) formula:

$$\varrho = \frac{n^2 f}{2(n^2-1)} \operatorname{ctg} i, \tag{4}$$

with f denoting the focal lenght of the collimator,

n — the refractive index for the line considered, and

i the angle of incidence, at minimum deviation (in the principal plane).

Fig. 5 shows the spectral line L, account being taken of the curvature. It will be here assumed that the admissible effective height l of the exit-slit is the one at

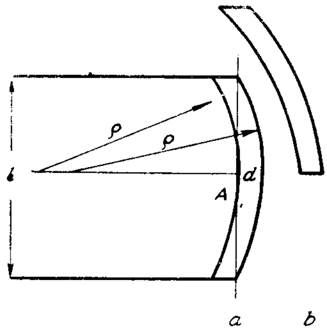

Fig. 5. Relating to definition of admissible effective height of exist-slit (admissible height of spectral line)

which the tangent A to the first edge of the line becomes the chord of the second one. Using a slit whose breadth is double that of the line, it is possible the comprise the latter entirely. By the theorem of Pitagoras,

$$l = 4\sqrt{\varrho^2-(\varrho-d)^2} \tag{5}$$

Neglecting d^2 with respect to $2\varrho d$, we have

$$l = 4\sqrt{2}\cdot\sqrt{\varrho d}. \tag{6}$$

The admissible *entrance-slit* height will be smaller in proportion to the magnifying factor of the spectrograph (for ИСП, this amount to about 1.5). If the exit-slit is several times wider than the line, then the admissible effective height is obtained by substituting the former's width for d in eq. (6). The paper by Gates (1952) brings a detailed computation of ϱ as function of the refractive index, for different angles of the prism. The following table has been prepared from Gates' graphs.

Table 2

	60° prism			45° prism
	n(quartz)	ϱ/f	for $f = 60$ cm	ϱ/f
1900 Å	1.65	0.5	$\varrho = 30$	1.00
2500 Å	1.6	0.6	36	1.05
4000 Å	1.55	0.7	42	1.15

ACTA PHYSICA POLONICA Vol. XIX (1960) Fasc. 3

It is seen that in direct spectrometry the prisms of smaller angle are of greater advantage. Computation yields the following results for the height of the exit-slit in the case of the ИСП 22 spectrograph:

Table 3

$\varrho = 35$ cm	d (microns)	l (mm)
	5	7.4
	10	10.4
	20	14.8
	40	20.8
	80	29.5
	100	33.0

The present author has carried out the computations for coincidence of the optical axis of the spectrometer and the centre of the entrance-slit. Were the axis to coincide with the edge of the slit, the admissible height would amount to one half of that computed (Fig. 5b). The correction γ as proposed by the author automatically for the inclination of the exit-slit accounts for deviation of the centre of the slit from coincidence with the optical axis of the spectrometer. Eq. (6) serves to determine experimentally the radius of curvature. For this, we proceed to find the difference in height between two positions of the camera that yields a difference in position of the centres of the profiles equal to the width of profile of the spectral line. That difference in height, when read on the scale of the arrangement for vertical displacement of the plates, will equal $l/2$. Then eq. (6) will yield the radius of curvature. From the theoretical point of view the line-width adopted and the way the width has beenn defined are not essential. Practically this will affect nothing but the degree of accuracy in measuring the radius of curvature.

Since in direct -reading spectrometry it is of importance that the recorded frequency of counting be maximum, and since this is in proportion with the area of the entranceslit, it seems of interest to consider *the problem of an exit-slit with curvature.* Let ϱ_1 and ϱ_2 denote the radii of curvature of the slit and the line, respectively. The height of the slit as in the situation of Fig. 6 will be assumed to be still admissible, if the slit and the line have the same width. From eq. (6), with the notation x instead of d (the latter is to denote the line-width ontly), we have:

$$l = 4\sqrt{2\varrho_1 x} \tag{7}$$

and

$$l = 4\sqrt{2\varrho_2 (x + d)}. \tag{8}$$

On eliminating x between both equations, we have

$$l = 4\sqrt{\frac{2\varrho_1 \varrho_2 d}{\varrho_1 - \varrho_2}}. \tag{9}$$

ACTA PHYSICA POLONICA Vol. XIX (1960) Fasc. 3

The latter is a generalisation of eq. (6), to which it reduces by substitution of $\varrho_1 = \infty$. If $\varrho_1 \approx \varrho_2$, and denoting the mean value of the radius by ϱ and the difference $|\varrho_1 - \varrho_2|$ by $\Delta\varrho$, we have finally:

$$l = 4\varrho \sqrt{\frac{2d}{\Delta\varrho}}. \tag{10}$$

With $d = 10$ microns, $\varrho = 35$ cm and $\Delta\varrho = 2.5$ cm (corresponding to the range of 2000—2500 Å), we obtain $l = 3.8$ cm. What has been said above concerning eq. (6) still holds for eq. (10).

Finally, let us consider the divergence between a circle and a parabola of the same curvature. A spectral line is stricly, a section of a parabole .Tha equations of

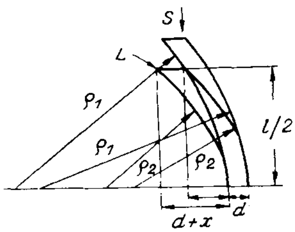

Fig. 6. Relating to definition of admissible effective height of exit-slit (with curved slit)

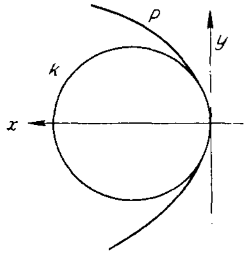

Fig. 7. Relating to computation of divergence between abscissae of circle and parabola

the circle and parabola are of the following form, respectively (cf. Fig. 7):

$$y_k^2 + (x_k - \varrho)^2 = \varrho^2;$$

$$y_p^2 = 2\varrho x_p.$$

The condition $y_k = y_p$ yields $x_k^2 + 2\varrho(x_p - x_k) = 0$. x_k is approximated from eq. (6). Finally, the following approximate formula is obtained:

$$x_k, - x_p = \frac{l^4}{8192 \cdot \varrho^3}. \tag{11}$$

With $\varrho = 35$ cm, the value of the difference begins to be of significance at $l = 25$ cm. It is seen cleary that the significance of substituting the parabola by a circle of the same radium of curvature is negligible.

The construction of curved slits is easily carried out by evaporation onto a quartz plate and subsequent incision (Polster 1951). The paper by Firestone and Randall (1938) deals with the construction of a curved slit of adjustable curvature. Fastie (1953) and Crosswile and Fastie (1954 and 1956) used 10 cm slits of 20 cm radius of curvature for grating spectrometers.

4. *Diffractional effect of neighbouring lines on recorded intensity*

It is a well-known fact that a spectral line results from a pattern of diffraction on the prism. Diffractions on the slit does not affect the resulting picture of the line in a way essential to our present considerations. The half-width of the zero order maximum is termed the "instrument line-width" and is given by the formula cited previously:

$$d = \frac{\lambda \sin \alpha}{\sin \beta} \tag{2}$$

wherein α is the angle of inclination of the beam with respect to the focal plane, and $\sin \beta$ — the relative aperture of the camera. The diffractional minima occur at a distance of the instrument width. From the Fresnel-Huygens principle, the consecutive approximate values of the diffractional maxima can be computed using the formula

$$A = \left(\frac{\sin \varphi/2}{\varphi/2}\right)^2, \tag{12}$$

wherein $\varphi = 2\pi n$. The following table contains the results up to order 500.

Table 4

n	A	n	A
0	1	9.5	1.1×10^{-3}
1.5	4.6×10^{-2}	10.5	9.0×10^{-4}
2.5	1.6×10^{-2}	15.5	4.3×10^{-4}
3.5	8.3×10^{-3}	20.5	2.4×10^{-4}
4.5	5.2×10^{-3}	30.5	1.0×10^{-4}
5.5	3.4×10^{-3}	50.5	4.0×10^{-5}
6.5	2.4×10^{-3}	100.5	1.0×10^{-5}
7.5	1.8×10^{-3}	200.5	2.5×10^{-6}
8.5	1.4×10^{-3}	500.5	4.0×10^{-7}

Consider the following example: let the recorded line be P 2136.199 Å and the perturbing one — the intense Cu 2135.976 Å line. These are wavelengths for which the dispersion of the ИСП 22 spectrograph amounts to 3.5 Å/mm, yielding a separation of 60 microns for the two lines. The instrument width of 6 microns enters 60 microns ten times. If the width of the exit-slit is 20 microns, then the slit stretches over orders from 7 to 12 of Cu 2135.976 Å. To compute the number of orders comprised, the slit should be projected upon the focussing plane along the beams perpendicular to the slit. Hence in the example under consideration not 3 but 5 orders are comprised. Thus, the effect of the Cu line will amount to something like an additional $5^0/_{00}$ of the Cu line intensity. If the last line is of an intensity of e. g. 100 times that of the P line, then one half of of the effect recorded is due to diffractiona

ACTA PHYSICA POLONICA Vol. XIX (1960) Fasc. 3

perturbation. The problem arises of how to account for the effect under consideration. It would seem right to introduce appropriate corrections for the perturbating line, accounting for its distance from the line measured, as well as for other factors. However, it would seem more correct to proceed along the following lines; Table 4 shows the effect of diffraction to be solely a quadratic diminishing function of the order of the spectrum. This effect is, thus, a far-reaching one. A number of neighbouring lines affect the line recorded, yielding a certain background. Hence the most correct approach consists in giving the effect of diffraction the treatment of a background. The background may be considered to be due largely to diffraction.

5. *Conclusions*

The foregoing cosiderations lead to the conclusions that, although the demand for high luminosity in photoelectric spectrometers is consistent, their construction should fulfill somewhat different conditions than those observed in the construction of spectrographs. Since the slit is to comprise the line with excess, it is possible partly to renounce conformily in favour of high liminosity. It may be of advantage to use high slits, high 45° prisms (instead of the 60° prisms commonly in use) having great focal lengths, and cylindrical lenses. With these conditions, higher luminosity and a greater radius of curvature will be obtained.

The author wishes to thank Professor Dr L. Jurkiewicz for his critical remarks and his valuable discussions.

REFERENCES

Bryon, F. R., Nahstoll, G. A., *JOSA*, **38**, 510 (1948).
Carlsson, C., *Spectrochem. Acta*, **6**, 211 (1954).
Crosswhile, H. M., Fastie, W. S., *JOSA*, **44**, 349 (1954).
Crosswhile, H. M., Fastie, W. S., *JOSA*, **46**, 110 (1956).
Fastie, W. S., *JOSA*, **42**, 641 (1952), **42**, 647 (1952); **43**, 1174 (1953).
Firestone, F. A., Randall, H. M., *Rev. sci. Instrum.*, **9**, 404 (1938).
Gates, A., *Jour. Phys.*, *20*, 275 (1952).
Rupert, C. S., *JOSA*, **42**, 779 (1952).
Hagenmah, N. D. *Z. angew. Phys.*, **6** 318 (1954).
Hanau, H., Wolfe, R. A., *JOSA*, **38**, 377 (1948).
Hulton, Müller, *Ark. Fys.*, **3**, 393 (1952).
Kayser, *Handbuch der Spektroskopie*, Leipzig (1900).
Minkowski, R., *Astrophys. J.*, **96**, 306 (1942).
Naish, J. M., *J. sci. Instrum.*, **28**, 138 (1951).
Naish, B., Ramsden, W., *Spectrochem., Acta*, **5**, 295 (1953).
Mostyn, R., Jury, R. V., *Spectrochem., Acta*, **5**, 257 (1953).
Ostrowski, K. W., *Acta phys. Polon.*, **18**, 231 (1959).
Polster, A., *JOSA 41*, 290 (1951).
Prokofiev, W. K., *Fotograficheskie metody kolichestviennovo spektralnovo analiza metallov i splavov*, Vols. I, II, (Moskva 1951).
Sawyer, R. L., *Experimental Spectroscopy*, N. Y. 1951 II. Ed.
Soda, M. S., *J. sci. industr. Res.*, **12 B**, 563 (1953).

ACTA PHYSICA POLONICA Vol. XIX (1960) Fasc. 3