

Article

A New Intensity Adjustment Technique of Emission Spectral Analysis When Measured at the Upper Limit of the Dynamic Range of Charge-Coupled Devices

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Abstract: The article presents a method of mathematical correction to be applied to the results of measuring the intensity of spectral lines using charge-coupled devices (CCDs) in the presence of the blooming effect. This technique is particularly applicable in atomic emission spectroscopy. It enables expansion of the dynamic range of spark emission spectrometers and significantly minimizes the result distortions of the measurements taken in the area of high element concentrations. The authors devised a mathematical model and proposed an algorithm to adjust the measured intensity of analytical lines at the photo detector upper limit, in addition to an algorithm for processing data from the spectra recording system. The proposed mathematical algorithm was integrated into the software for the SPAS-02 and SPAS-05 spark spectrometers produced in Russia, and tested in determining the chemical composition of steels. The findings show that the actual dispersion of the analytical line intensity distribution may exceed the measured dispersion by a factor of 1.5, and their intensities may differ by a factor of 2. This algorithm may be implemented in atomic emission spectrometer software and makes it possible to adjust the calibration curves for a range of high alloying element concentrations when the analytical line intensity is at the upper limit of the CCD dynamic range.

Keywords: calibration; charge-coupled image sensors; impurities; metrology; plasma devices; spectral analysis; spectroscopy



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1. Introduction

Both linear and matrix charge-coupled devices (so-called CCDs) are widely utilized in various tools for measuring light flux intensity of different frequency ranges [1–7]. However, they have a considerably lower dynamic range compared to photo-detectors such as photo-multipliers. Due to this fact, it is often necessary to measure light flux intensity at the upper limit of the dynamic range, which, as presented below, leads to serious distortions in measurement results due to blooming [8–10]. This necessitates the development of various expansion techniques of the CCD dynamic range [11–13].

In particular, this issue applies to emission spectroscopy, a widespread elemental composition estimation method [14,15]. The dynamic range of the CCDs used in emission spectrometer recording systems does not exceed the value of the order of a few units of 10^4 . This is often insufficient for the study of certain types of objects. Since most emission spectrometers use gas-discharge plasma, the measuring limit on the low-end concentration is due to intrinsic plasma emission noise, and on the high-end concentration it is due to the charge limit that a CCD can accumulate in a single element (pixel) without affecting neighboring elements. As a rule, it is the weak signals to which special attention is paid [16–18], and measurements at the upper limit of the dynamic range are not sufficiently studied from the methodological point of view. When using CCD tools in emission spectroscopy, changes

in intensity should be adjusted for at certain wavelengths (that is, only in individual pixels of the CCD rather than in the entire CCD). To the best of our knowledge, no such technology is currently available. In this study, we attempted to develop a mathematical algorithm that allows for adjusting the intensity recorded by individual CCD pixels subject to the blooming effect. It does not require any changes in the parameters of the spectrometer.

The elemental composition analysis using emission spectrometers occurs under certain spectrum excitation system parameters, signal accumulation times, and sampling methods, which are selected individually for a certain type of samples. This set of circumstances is commonly referred to as the analytical technique.

Often, a single technique requires determining the impurity level within a concentration range that is of the order of, or greater than, the dynamic range of the spectrometer recording system. During the recording time, a charge is accumulated in CCD pixels. This causes the blooming effect. Its essence is that when a certain value of this charge is exceeded, its electric field begins to affect neighboring pixels; the image of the analytical line begins to “blur”, and its amplitude ceases to increase (see Figure 1 as an example). This is what is known as the integral upper limit of time intensity, which this recording system can record.

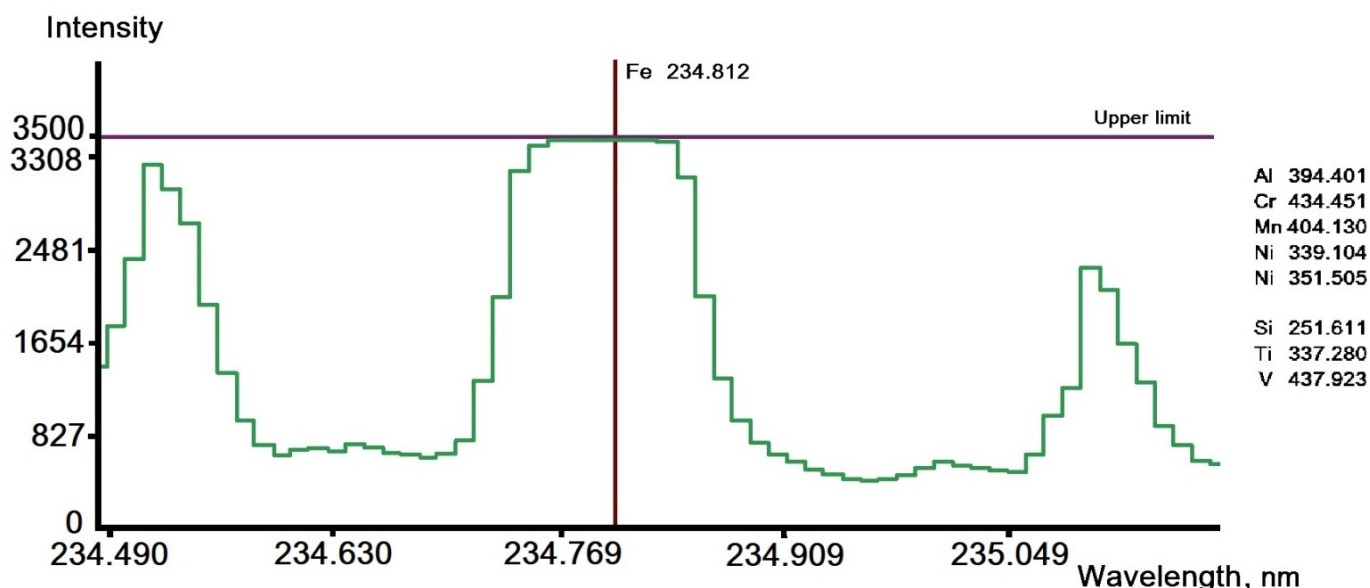


Figure 1. An example of recording the Fe 234.812 spectral line under recording conditions in which its recorded intensity exceeds the upper CCD limit. It shows a view of the software window of the SPAS-02 emission spectrometer (<http://activespectr.com/en/products/emission-spectrometers/optical-emission-spectrometer-oes-spas-02-metal-analysis> (accessed on 27 February 2022)). The spectral resolution is about 0.05 nm. A fragment of the recorded spectrum of the UG0i (low-alloy steel) sample with an integration time of 16 ms is shown; the type of discharge is a low-voltage spark in an argon atmosphere.

Thus, in order to determine trace concentrations of impurity elements one has to select spectrum excitation parameters and the signal accumulation time, so that it is possible to record weak (due to the low concentration of corresponding atoms in plasma) analytical lines. If spectrum excitation parameters of the source are the same but the impurity content in a sample and/or signal accumulation time are higher, it may be necessary to record the intensity at the value corresponding to its limit. This evidently leads to the underestimation of the measured analytical line intensity compared to its true value.

As an example, Figure 2 shows data for identifying Al in Fe-based alloys when its concentration varies within a wide range (from 0.003 to 10%). The analytical line Al I 394.4 nm and the reference line Fe I 389.57 nm were used. The spectrometer used was the SPAS-05 (<https://spas05.com/en/products/emission-spectrometers/optical-emission->

[spectrometer-oes-spas-05-metal-analysis](https://spas05.com/en/products/emission-spectrometers/optical-emission-spectrometer-oes-spas-05-metal-analysis) (accessed on 27 February 2022)), the type of discharge was a low-voltage spark in an argon atmosphere, and the integration time was 16 ms. It can be seen that, with an increase in concentration above 1%, the slope of the calibration curve (curve 3) begins to drop sharply.

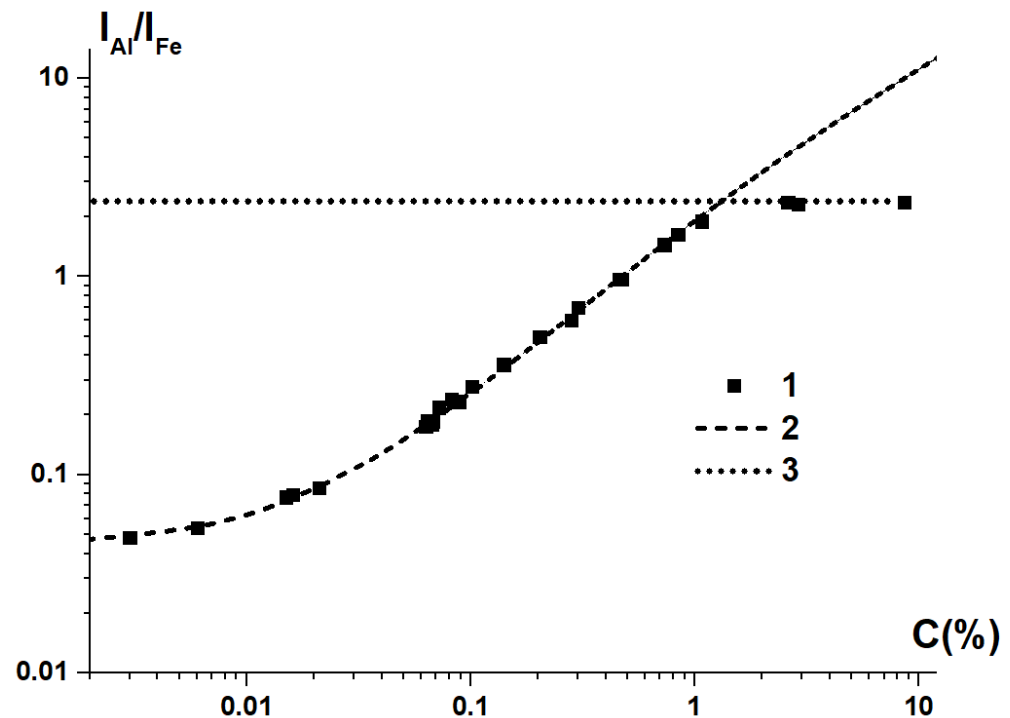


Figure 2. The influence of the limiting integral intensity of the CCD (denoted as $(I_{Al} / I_{Fe})_{lim} - 3$), on the dependence of the relative intensity I_{Al} / I_{Fe} of the analytical line Al I 394.4 nm (reference line—Fe I 389.57 nm) on the Al concentration in Fe-based alloys; 1—processing data from the CCD receiver according to the usual method; 2—calibration curve for the range of relative concentrations up to 1%. The SPAS-05 spectrometer. The logarithmic scale is used. (<https://spas05.com/en/products/emission-spectrometers/optical-emission-spectrometer-oes-spas-05-metal-analysis> (accessed on 27 February 2022)); samples from the sets UG0k–UG9k (low-alloy steels), LG57–LG68 (high-alloy steels), RG25a–RG31a (low-alloy steels), RG10–RG18 (high-speed steels), and IARM-39B (low-alloy steel) were used. The analysis was carried out using the SPAS-05 emission spectrometer; the discharge type was a low-voltage spark in an argon atmosphere.

The existing methods of tackling the blooming effect are mainly based on electronic methods of changing voltages in the CCD signal reading system [19,20] or methods of removing excess electrons from the pixels using additional electrical circuits [21]. They are widely used in imaging with CCD receivers, but they are not applicable for quantitative measurements of intensities when the image projected on the CCD (consisting of a large number of pixels) contains pixels with and without blooming at the same time.

Another way to remove the blooming effect implies using two CCD receivers receiving the same image [9]. One of them has a short signal integration time and is used when the blooming effect appears, while the second one having a long integration time is used at a relatively low intensity. This method is convenient for obtaining video images with a wide range of variation in the radiation intensity; however, its use in emission spectrometers significantly complicates the design of the optical unit of the spectrometer.

The proposed method for adjusting the intensity of the spectral line allows increasing the measured radiation intensity by a factor of 2 despite the presence of the blooming effect without changing the circuitry for reading the signal from the CCD.

2. Materials and Methods

Key formulas. Let us consider an algorithm for measuring the line intensity using a CCD in emission spectrometers. Intensity is measured repeatedly (each measurement will be called a “frame”), and in each frame during a certain time (frame duration), the signal is integrated. Due to the random nature of emission of radiation by atoms, with its sufficiently high intensity, the values of the charge accumulated by the pixels for some frames are higher than the upper limit of the CCD. As a result, their measured intensity, which is equal to the upper limit of the CCD, becomes lower than the actual one. However, the intensities of the remaining frames (which are below the upper limit of the CCD) are measured accurately, to a certain extent, and distributed according to a certain statistical law. The task is to use the array of measured frame intensities and the fact that all real intensities of each frame obey one statistical law to restore the real average intensity of the analytical line and its variance, which are calculated for all registered frames.

Our aim is to restore the real intensity of the spectral line as an average of a certain number of frames using frames whose intensity as a statistically variable parameter did not exceed the threshold after which the blooming effect manifests itself. In this sense, the proposed intensity adjustment method is mathematical rather than instrumental.

It is well known that the substance analysis for the content of a certain element is carried out in emission spectrometers with the so-called calibration curves—the dependences of intensities I (absolute or relative, depending on the analytical technique) on an impurity level C in a sample:

$$I = I(C). \quad (1)$$

The dependence of the relative intensity of the analytical line **Al I** 394.4 nm (reference line—**Fe I** 389.57 nm) on the concentration C of aluminum in steels that is shown in Figure 2 has the following form:

$$\frac{I_{Al}}{I_{Fe}} = -0.019C^3 + 0.443C^2 + 0.049C - 6.79 \times 10^{-4} + \frac{0.001}{1 + C^5}. \quad (2)$$

A benchtop spark emission spectrometer with the following characteristics was used in the research to analyze alloys:

- type of discharge—low-voltage spark in an argon atmosphere;
- spectral resolution—no more than 0.05 nm;
- optical configuration—Paschen–Runge;
- spectral range—170–450 nm;
- recording system—8 CCD TCD1304DG.

The effect considered above leads to the fact that, in the area of high concentrations, derivative $\frac{dI}{dC}$, decreases (or it can be said that the derivative $\frac{dC}{dI}$ increases), which negatively affects the quality of the measurements (see Figure 2) due to an increase in both random and systematic errors.

Thus, studying the adjustment possibility of the analytical line intensity when measured by CCD recording systems at the upper limit of the analytical signal seems to be highly relevant.

To avoid uncertainty, we consider linear CCDs. Let the analytical line image in the focal plane of a linear CCD spectrograph take L pixels. We first consider some arbitrary pixel number n . Taking into account the set task, first, we are interested in the pixels at the maximum of the analytical line.

As is well known, the algorithm of CCD signal accumulation in an individual pixel can be described as follows: the signal is accumulated for some time, called the accumulation time, after which it is read out, digitized, and summed with the previous signals. After completing a certain number of cycles, called the frame count, the stack is divided by the number of frames. This is the measured signal in the given pixel.

Let the frame count be $M \gg 1$, and the distribution density of by-frame intensity probabilities (i.e., not the measured but the actual intensity) that goes into pixel n , obeys a Gaussian distribution:

$$P_n(I_{nk}) = A_n \exp \left[-\frac{(I_{nk} - \bar{I}_n)^2}{2\sigma_n^2} \right] \quad (3)$$

where I_{nk} is the intensity value during the k frame in pixel n ; σ_n is the standard deviation of the average value for the frame-by-frame distribution of $P_n(I_k)$ in pixel n ; $\bar{I}_n = \frac{1}{M} \sum_{k=1}^M I_{nk}$ is the average intensity value for M frames in pixel n ; A_n is the normalization constant.

I_{nk} varies within the limits:

$$I_{nk} \in [I_{nN}, \infty); I_{nN} \ll \bar{I}_n, \quad (4)$$

where I_{nN} is some sufficiently small value of the order of plasma background radiation intensity at a wavelength, corresponding to the location of pixel n .

We assume that this CCD maximum allowable intensity does not depend on a pixel number and is equal to I_{max} . We also assume that the measurement results in some average intensity $\bar{I}_{nm}$.

The qualitative considerations clarify that if $\bar{I}_n$ is significantly less than I_{max} , the values $\bar{I}_n, \bar{I}_{nm}$ will be close. When $\bar{I}_n$ approaches the value of I_{max} , the frames in which the pixel is exposed to radiation of an intensity exceeding I_{max} will have I_{max} as a measurement result. Thus, $\bar{I}_{nm} < \bar{I}_n$.

This circumstance must be taken into account when taking measurements. In this regard, it is necessary to find the correlation between the values $\bar{I}_{nm}, \sigma_n$, and $\bar{I}_n$. Following Appendix A, we obtain the correlation of the actual intensity and the relative dispersion $\bar{I}_n, \sigma_n$, with the measured values $\bar{I}_{nm}, \sigma_{nm}$ (see the definitions of values $b_{nm}, \Sigma_n, \alpha_{nm}, \Sigma_{nm}$ in Appendix A):

$$b_{nm} \left[1 + \operatorname{erf} \left(-\frac{\alpha_{nm} - b_{nm}}{\sqrt{2}\Sigma_n b_{nm}} \right) \right] - \frac{\Sigma_n \alpha_{nm}}{\sqrt{2}\pi} \exp \left[-\left(\frac{\alpha_{nm} - b_{nm}}{\sqrt{2}\Sigma_n b_{nm}} \right)^2 \right] + \alpha_{nm} \left[1 - \operatorname{erf} \left(-\frac{\alpha_{nm} - b_{nm}}{\sqrt{2}\Sigma_n b_{nm}} \right) \right] = 1, \quad (5)$$

$$\frac{\Sigma_{nm}^2}{b_{nm}^2} = \Sigma_n^2 \left[1 - \frac{1}{\sqrt{\pi}} \Gamma \left(\frac{3}{2}, \frac{\alpha_{nm} - b_{nm}}{\sqrt{2}\Sigma_n b_{nm}} \right) \right] - \sqrt{\frac{2}{\pi}} \Sigma_n (b_{nm} - 1) \exp \left[-\left(\frac{\alpha_{nm} - b_{nm}}{\sqrt{2}\Sigma_n b_{nm}} \right)^2 \right] + \frac{(b_{nm} - 1)^2}{2} \left[1 + \operatorname{erf} \left(-\frac{\alpha_{nm} - b_{nm}}{\sqrt{2}\Sigma_n b_{nm}} \right) \right] - \frac{1}{2} \left[1 - \operatorname{erf} \left(-\frac{\alpha_{nm} - b_{nm}}{\sqrt{2}\Sigma_n b_{nm}} \right) \right]$$

when $\alpha_{nm} \geq b_{nm}$;

$$\frac{\Sigma_{nm}^2}{b_{nm}^2} = \frac{\Sigma_n^2}{\sqrt{\pi}} \Gamma \left(\frac{3}{2}, \frac{b_{nm} - \alpha_{nm}}{\sqrt{2}\Sigma_n b_{nm}} \right) - \sqrt{\frac{2}{\pi}} \Sigma_n (b_{nm} - 1) \exp \left[-\left(\frac{\alpha_{nm} - b_{nm}}{\sqrt{2}\Sigma_n b_{nm}} \right)^2 \right] + \frac{(b_{nm} - 1)^2}{2} \left[1 + \operatorname{erf} \left(-\frac{\alpha_{nm} - b_{nm}}{\sqrt{2}\Sigma_n b_{nm}} \right) \right] - \frac{1}{2} \left[1 - \operatorname{erf} \left(-\frac{\alpha_{nm} - b_{nm}}{\sqrt{2}\Sigma_n b_{nm}} \right) \right]$$

if $\alpha_{nm} < b_{nm}$, where $\Gamma(a, x) = \int_x^\infty t^{a-1} \exp(-t) dt$ is the gamma function; $\Sigma_n = \frac{\sigma_n}{\bar{I}_n}$ is the relative dispersion of the actual intensity; $b_{nm} = \frac{\bar{I}_n}{\bar{I}_{nm}}$; $b_{nm} \geq 1$; $\alpha_{nm} = \frac{I_{max}}{\bar{I}_{nm}} > 1$.

Thus, Equation (5) represent the desired system of equations in order to obtain the actual intensity and density dispersion of its distribution probability.

The next thing to consider is that the analytical line image on a CCD has a finite width (at the base) which, in modern emission spectrometers, ranges from 3 to 10 pixels. The width depends on the linear dispersion of the spectrograph, the CCD type, and the optical circuitry (which determines the shape of the focal surface and, hence, the focusing degree of a particular CCD area).

3. Results

CCD recording systems are usually used in spectrographs based on the Paschen–Runge configuration [22,23]. Linear CCDs having the smallest possible horizontal pixel size

and the highest possible height are typically used in emission spectrometers. The latter is designed to increase the spectrometer recording system sensitivity. For example, a Toshiba TCD1304DG CCD with a pixel size of $8 \times 200 \mu\text{m}$ is very popular. Therefore, “SPAS”-05 emission spectrometers produced by Active Co., Ltd., Saint Petersburg, Russian, which use TCD1304DG CCD, have a spectrum resolution of up to 0.05 nm. The analytical line width of the intensity $(0.5 \div 0.7)I_{\text{max}}$ in the pixel corresponding to the spectral line center is about 6 to 7 pixels at the base, when the spectrum is spark-excited in argon atmosphere. The linewidth is determined both by the conditions in the plasma (Doppler and Lorentz broadening) and by the instrumental function of the spectrometer.

At a normal width of the entrance slit, the contribution of these factors is comparable. It should be noted that, in CCD emission devices that have the Paschen–Runge configuration, in addition to the natural width of the spectral line (Doppler line profile, which is associated with a high temperature, and Lorentzian shape, which is associated with the finite lifetime of the excited level), there is one more reason for line-broadening: it is due to the fact that linear CCDs that are used have a flat shape, whereas the focal surface has a non-zero curvature. Because of this, at any position of the CCD relative to this surface, a maximum of two points of the receiver are in focus. The rest are inevitably out of focus.

Apparently, the closer the value $\bar{I}_{nm}$ is to I_{max} , the greater the difference will be between $\bar{I}_{nm}$ and $\bar{I}_n$. Due to this fact, the effect considered will be significant for the pixels that form the spectral line center. Earlier in the paper we designated the number of pixels constituting the intensity $\bar{I}_{nm}$, by $K < L$. We number them from left to right. Then, for the actual intensity of the spectral line:

$$\bar{I}_{0r} = \sum_{n=1}^K \bar{I}_n = \frac{1}{M} \sum_{n=1}^K \sum_{k=1}^M I_{nk} \quad (6)$$

we obtain the correlation:

$$\bar{I}_{0r} = \sum_{n=1}^K \bar{I}_{nm} b_n(\bar{I}_{nm}, \Sigma_{nm}), \quad (7)$$

where $b_n(\bar{I}_{nm}, \Sigma_{nm})$ is found from Equation (5).

Thus, the algorithm for applying the results obtained when used to measure spectral line intensities is as follows. Cyclic signal accumulation occurs during the recording process simultaneously in each pixel of the CCD for a period of time, called a frame. The analog signal is then read out and sent to the ADC, where it is converted into digital format. Furthermore, there is an accumulation during the subsequent frames. As stated previously, to improve the measurement statistics (to reduce the root-mean-square value—RMS), the number of frames M usually exceeds 100 depending on the measurement technique.

It should be noted that when working with relative intensities, when it is also necessary to calculate the intensity of the reference line (i.e., the properly selected base line), it is sufficient to perform adjustment according to the designed procedure only for the analytical line of the impurity or alloying element. The reference line intensity weakly depends on their concentration and, in advance, is chosen to be not too large (as a rule, not more than $(0.5 \div 0.7)I_{\text{max}}$); otherwise, the adjustment is also needed for the reference line.

The aforementioned mathematical model is applied according to the following algorithm. The signal accumulated in each pixel constituting the analytical line intensity during each frame is saved. Thus, we have a dimensional dataset $M \cdot K$ for one analytical line. These data are used to calculate the values $\bar{I}_{nm}, \Sigma_{nm}$ by the formulas:

$$\bar{I}_{nm} = \frac{1}{M} \sum_{l=1}^M I_{nml}; \quad \Sigma_{nm} = \sqrt{\frac{1}{(M-1)\bar{I}_{nm}} \sum_{l=1}^M (I_{nml} - \bar{I}_{nm})^2}. \quad (8)$$

After that, System (5) is solved and the actual parameters $\bar{I}_n, \Sigma_n; n = 1, \dots, K$ are found for each of the pixels, constituting the analytical line intensities, which are used in calibration graph plotting.

4. Discussion

We consider the performance of the values $\bar{I}_n, \Sigma_n$ depending on the parameters $\bar{I}_{nm}, \Sigma_{nm}$. It is quite evident that when $\bar{I}_n + 3\sigma_n < I_{max}$ there will be the correlation $\bar{I}_n \approx \bar{I}_{nm}$. Indeed, according to the “three sigma” criterion, 99.73% of all actual frame intensity values will be equal to the corresponding measured intensity values. We can conclude now that as the dispersion σ_n decreases (if $\bar{I}_n < I_{max}$), the adjustment for the effect considered will decrease and vice versa. In this case, when the dispersion σ_n is fixed, the growth in the intensity $\bar{I}_n$ results in the adjustment upswing (the parameter b_{nm} upswing) and vice versa. In the limiting case when $\bar{I}_n < I_{max}$ and $\sigma_n \rightarrow 0$ or, equivalently, $\sigma_{nm} \rightarrow 0$, we obtain $\bar{I}_n \rightarrow \bar{I}_{nm}$. These dependencies also directly result from the solution of System (5).

We now consider the case in which $\bar{I}_n > I_{max}$. In this case, the difference between the measured spectral line intensity and the actual line intensity is higher than when $\bar{I}_n < I_{max}$. This happens because, with the increase in $\bar{I}_n$ in each pixel, some of the values $I_{nk} > I_{max}$ ($k = 1, 2, \dots, M$) when measured are unaffected by $\bar{I}_n$ and are replaced by I_{max} . The greater the frame dispersion σ_n and the closer $\bar{I}_{nm}$ to I_{max} , the greater the difference between $\bar{I}_n$ and $\bar{I}_{nm}$. This is illustrated by the data in Figures 3 and 4, which show the dependence of value $b_n\left(\frac{1}{\alpha_{nm}}, \Sigma_n\right)$ for a single pixel. It can be seen that when the relative actual by-frame dispersion is less than 10%, the adjustment is negligibly small if $\bar{I}_n < 0.95 \cdot I_{max}$. At the same time, if the dispersion $\Sigma_n = \frac{\sigma_n}{I_n}$ is up to 40%, the adjustment can be neglected only if $\bar{I}_n < 0.75 \cdot I_{max}$.

It should be noted that the actual dispersion σ_n is wider than the measured σ_{nm} . The reasons for this are discussed above. Apparently, when $\bar{I}_n$ (and therefore $\bar{I}_{nm}$) increases, this difference becomes greater.

Figures 5 and 6 represent the dependences $b_{nm}\left(\frac{1}{\alpha_{nm}}, \Sigma_{nm}\right)$, and Figures 7 and 8 show $\Sigma_n(\bar{I}_{nm}, \Sigma_{nm})$. As we predicted, as the parameter $\alpha_{nm} = \frac{I_{max}}{\bar{I}_{nm}}$ increases and the relative dispersion of the measured intensity increases, the parameter b_{nm} increases. The same can be said of the value Σ_n . After comparison of the data from Figures 3 and 5, we can conclude that, at the same parameter α_{nm} , the in-equation $b_{nm}\left(\frac{1}{\alpha_{nm}}, \Sigma_{nm}\right) > b_{nm}\left(\frac{1}{\alpha_{nm}}, \Sigma_n\right)$ is satisfied. As we stated previously, this results from the fair correlation $\Sigma_n > \Sigma_{nm}$.

Above, we discussed the effect of reducing the measured intensity for a single pixel. When we analyze how this effect interferes with the spectral line intensity measurement, we must remember that the intensity adjustment in different pixels will be different. To illustrate the developed algorithm, we consider the situation in which the spectral line according to the measurements has a Doppler shape. We want to emphasize that the specific form of the measured spectral line intensity in this case is of no crucial significance.

We can state that the half-width of the actual spectral line will be narrower, and the width at the base will be the same. This is true if, during the signal accumulation time in each pixel, the accumulated charge does not affect the neighboring pixels. Indeed, the analysis shows that, if the relative by-frame dispersion is the same, the intensity adjustment decreases with the reduction in the intensity itself. Thus, the adjustment results in a more significant increase in the intensity of the central pixels of the image rather than the intensity of the pixels on the spectral line wings. This will decrease the half-width of the line.

The line width at the base remains the same because, for the image forming edge pixels with low intensity, compared to I_{max} , the adjustment for the effect considered is negligibly small.

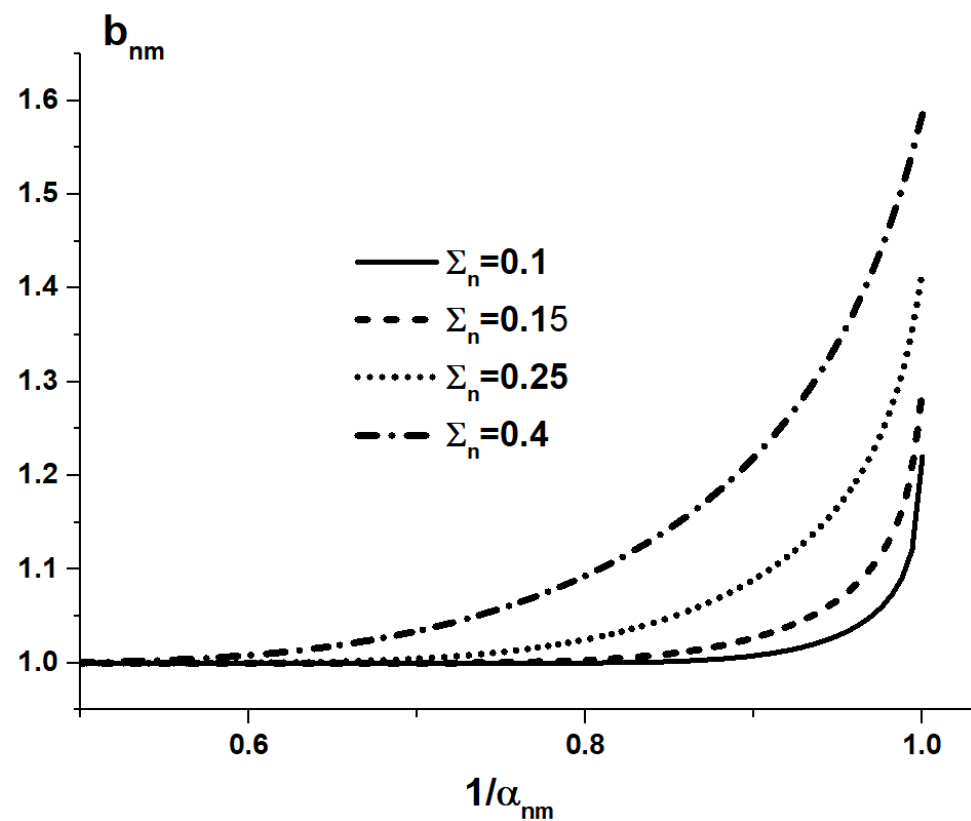


Figure 3. Intensity ratio dependency in a single CCD pixel $b_{nm} = \frac{\bar{I}_n}{\bar{I}_{nm}}$ on parameter $\alpha_{nm} = \frac{I_{max}}{I_{nm}}$ at various relative dispersions of the actual intensity.

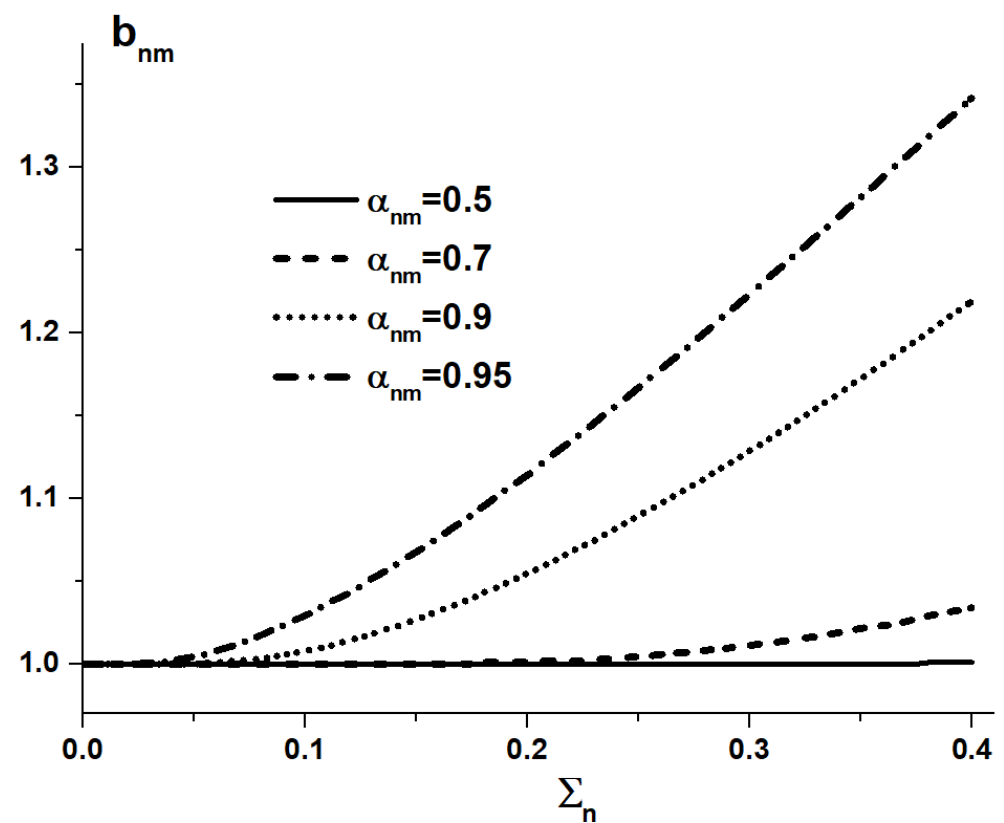


Figure 4. Intensity ratio dependency in a single CCD pixel $b_{nm} = \frac{\bar{I}_n}{\bar{I}_{nm}}$ on the relative dispersion of the actual intensity Σ_n with the various parameters α_{nm} .

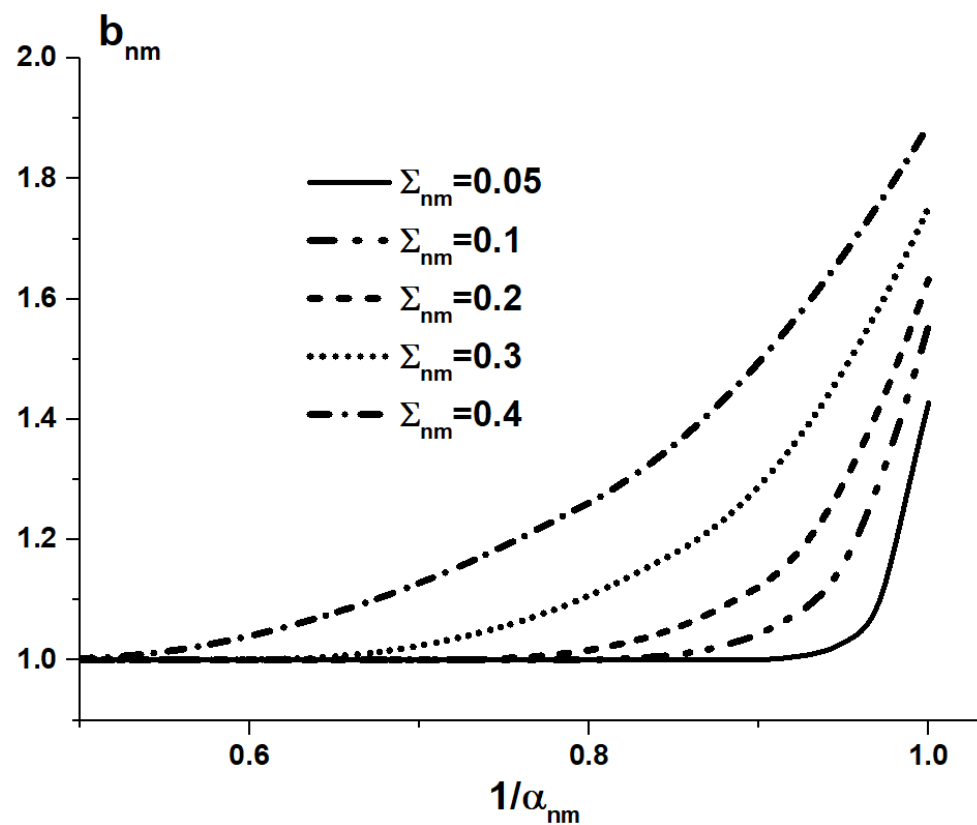


Figure 5. Intensity ratio dependency in a single CCD pixel $b_{nm} = \frac{\bar{I}_n}{\bar{I}_{nm}}$ on parameter $\alpha_{nm} = \frac{I_{max}}{I_{nm}}$ at various relative dispersions of the measured intensity.

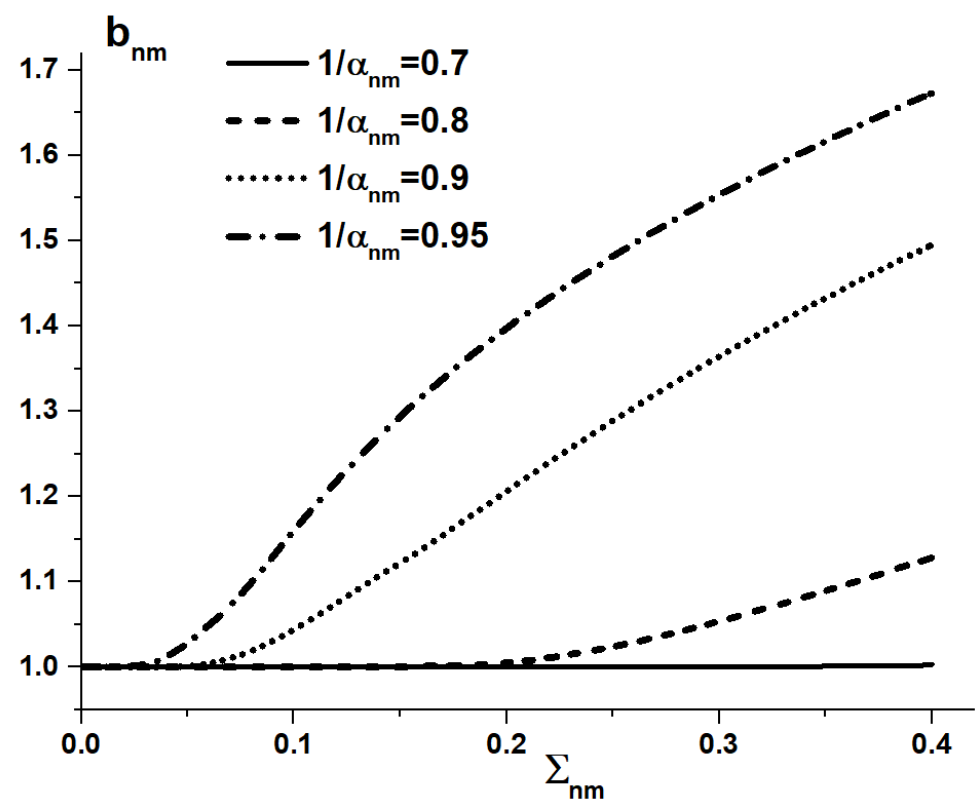


Figure 6. Intensity ratio dependency in a single CCD pixel $b_{nm} = \frac{\bar{I}_n}{\bar{I}_{nm}}$ on the relative dispersion of the measured intensity Σ_{nm} with the various parameters.

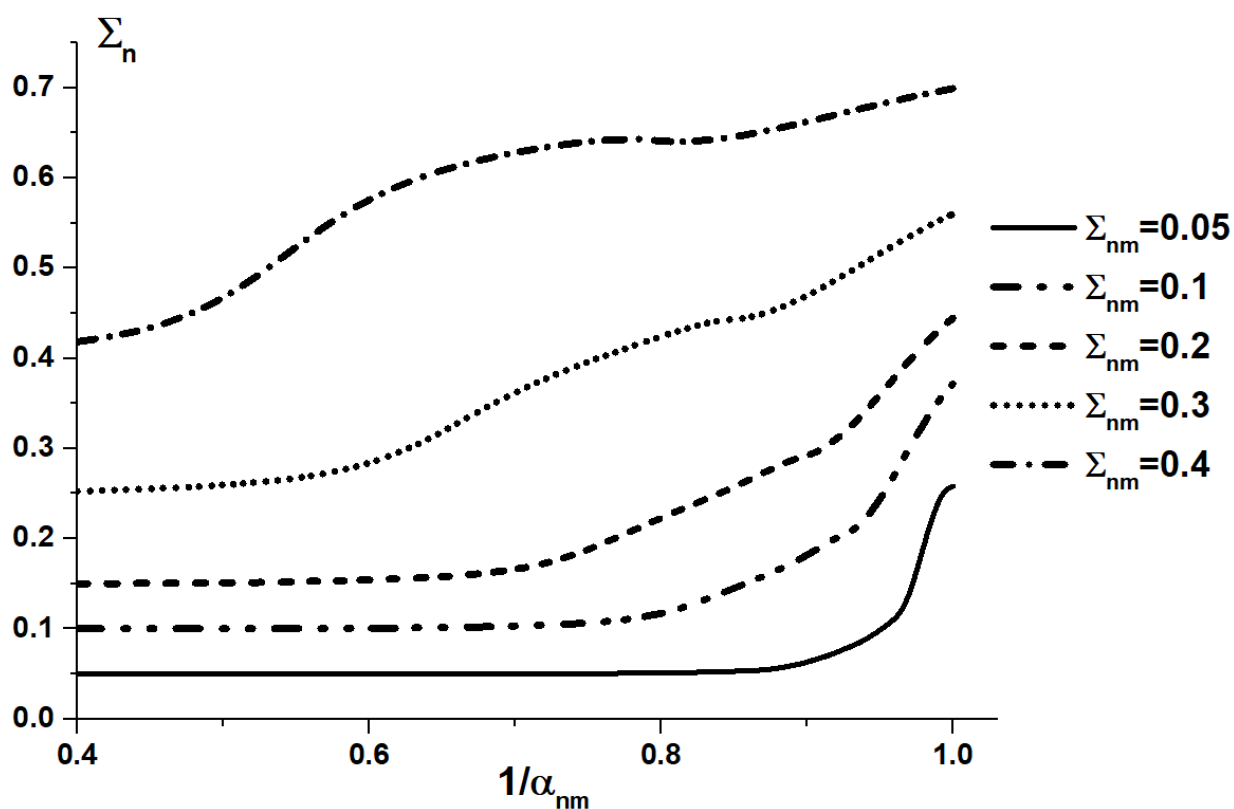


Figure 7. The dependency of the relative dispersion of the actual intensity in a single CCD pixel Σ_n on parameter α_{nm} at various dispersions of the measured intensity Σ_{nm} .

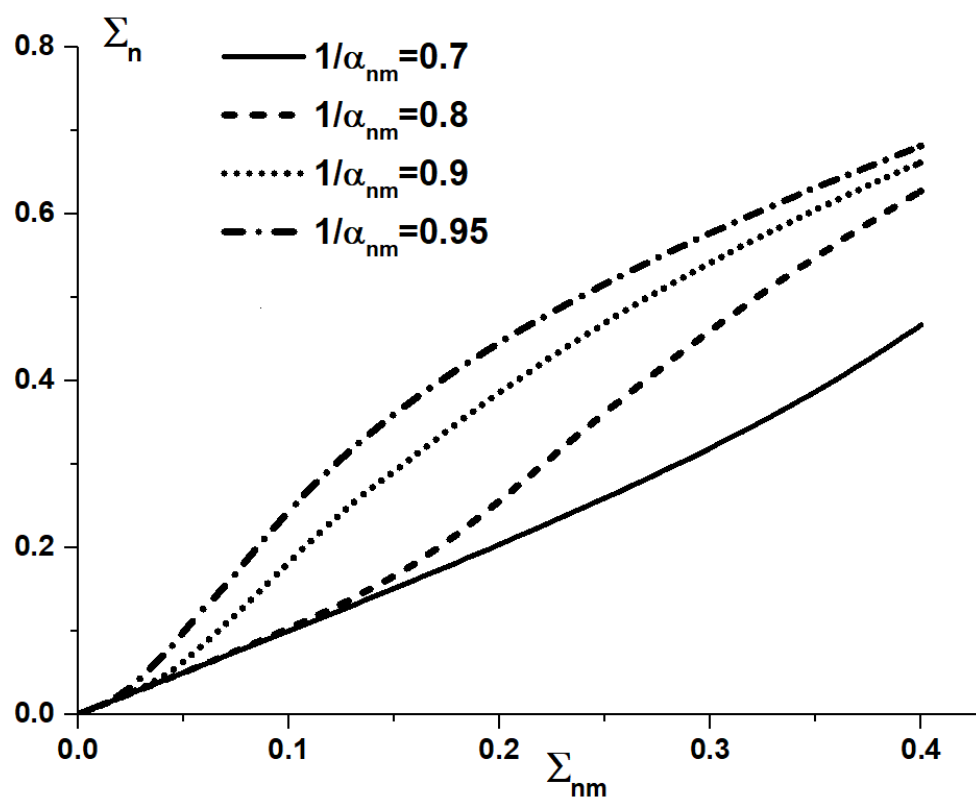


Figure 8. The dependency of the relative dispersion of the actual intensity in a single CCD pixel Σ_n on the dispersion of the measured intensity Σ_{nm} at the various parameter values α_{nm} .

We assumed previously that the measured spectral line width in pixels at the base is equal to L . We now number these pixels from right to left from 1 to L . Moreover, we assume, for simplicity, that the center of the spectral line coincides with the center of one of the pixels, i.e., number L is odd. Based on the line width at the base, we understand that this number of pixels, when the intensity is measured in the first and the last (number L) pixels, is 10^{-3} of the intensity in the center. This assumption is supported for modern emission spectrometers used for the analysis of, for example, metals and alloys, and the lines with the measured intensity in the central pixel of the order of value I_{max} .

As we noted previously, when developing an analytical technique for calculating analytical line intensities with spectrometer software where CCDs are used as radiation receivers in the recording system, it is necessary to indicate the pixels whose intensities should be summed. Figure 9 shows, as an example, a view of the corresponding window of the SPAS-02 emission spectrometer software (<http://activespectr.com/en/products/emission-spectrometers/optical-emission-spectrometer-oes-spas-02-metal-analysis> (accessed on 27 February 2022)) designed to analyze metals and alloys (pixels inside the yellow shading on the line Ni 351.505 nm). As can be seen, the summed pixels occupy almost the entire line width for low Ni concentrations (of a weak line), whereas, for high concentrations, they occupy only the central pixels, as the width of the line image increases with its intensity. Thus, the in-equation $L > K$ is usually satisfied. If the intensity constituting pixels symmetrical to the center of the line is chosen, number K will also be odd.

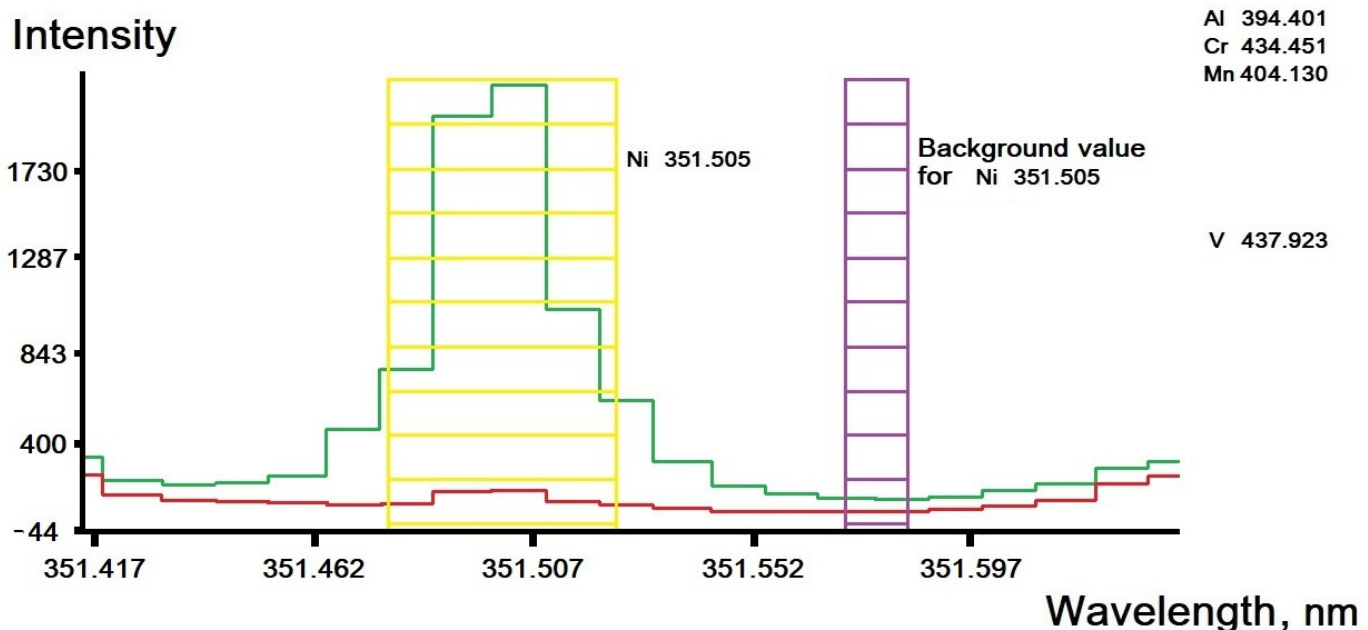


Figure 9. A view of the corresponding window of the software used in the SPAS-02 emission spectrometer (<http://activespectr.com/en/products/emission-spectrometers/optical-emission-spectrometer-oes-spas-02-metal-analysis> (accessed on 27 February 2022)) in the area of the analytical line Ni 351.505 nm; the red line shows the standard sample of low-alloy steel 1104 with a Ni content of 0.094%; the green line shows the standard sample of low-alloy steel 1101 with a Ni content of 3.34%. When determining the intensity of the line, the signals from the pixels located inside the yellow shading are summed.

For the measured intensity in pixel n we have:

$$\bar{I}_{nm}(n) = I_0 \exp \left\{ - \left[\frac{n - \frac{(L-1)}{2}}{\Delta} \right]^2 \right\}; \quad \Delta = \frac{(L-1)}{2\sqrt{3 \cdot \ln(10)}}, \quad (9)$$

and for the line measured intensity we obtain:

$$\bar{I}_{0M} = I_0 \sum_{n=\frac{L-K}{2}+1}^{\frac{L+K}{2}} \exp \left\{ - \left[\frac{n - \frac{(L-1)}{2}}{\Delta} \right]^2 \right\}. \quad (10)$$

Consequently, for the actual intensity of the spectral line we obtain:

$$\bar{I}_{0r} = I_0 \sum_{n=\frac{L-K}{2}+1}^{\frac{L+K}{2}} \exp \left\{ - \left[\frac{n - \frac{(L-K)}{2}}{\Delta} \right]^2 \right\} b_{nm}; \quad b_{nm} = b_{nm} \left(\exp \left\{ - \left[\frac{n - \frac{(L-1)}{2}}{\Delta} \right]^2 \right\}, \Sigma_{nm} \right). \quad (11)$$

For simplicity, we assume that the relative dispersions Σ_{nm} are unrelated to the frame number and equal to value Σ_{0m} .

Figure 10 shows Formulas (9)–(11) for calculating the dependency of value $b_0 = \frac{\bar{I}_{0r}}{\bar{I}_{0M}}$ for $L = 7$ and $K = 3$ (typical values for modern emission spectrometers designed to analyze metals and alloys) on parameter α_{4m} (i.e., parameter α_{nm} calculated for the central pixel, which, if $L = 7$, is number 4) at different relative dispersions Σ_{0m} . Comparing these data with the data in Figure 5 shows that, all other things being equal, the inequation is satisfied:

$$b_0 < b_{4m}$$

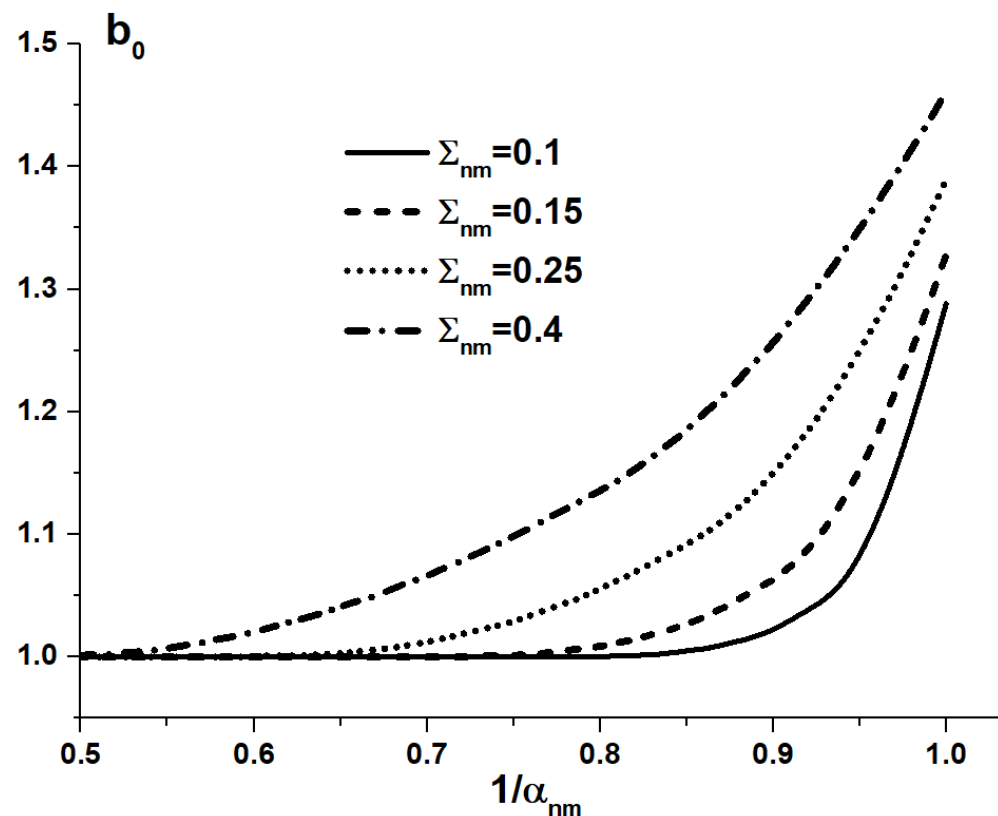


Figure 10. Intensity ratio dependency of the spectral line $b_0 = \frac{\bar{I}_{0r}}{\bar{I}_{0M}}$ on parameter $\alpha_{nm} = \frac{I_{max}}{I_{nm}}$ at various relative dispersions of the measured intensity; $L = 7$; $K = 3$.

The same can be said of the value b_0 calculations, shown in Figure 11 (depending on Σ_{0m} at different values of α_{4m}). The reason for this, as previously discussed, is that, when moving away from the center of the line, the effect considered decreases due to a decrease in the intensity in the corresponding pixels.

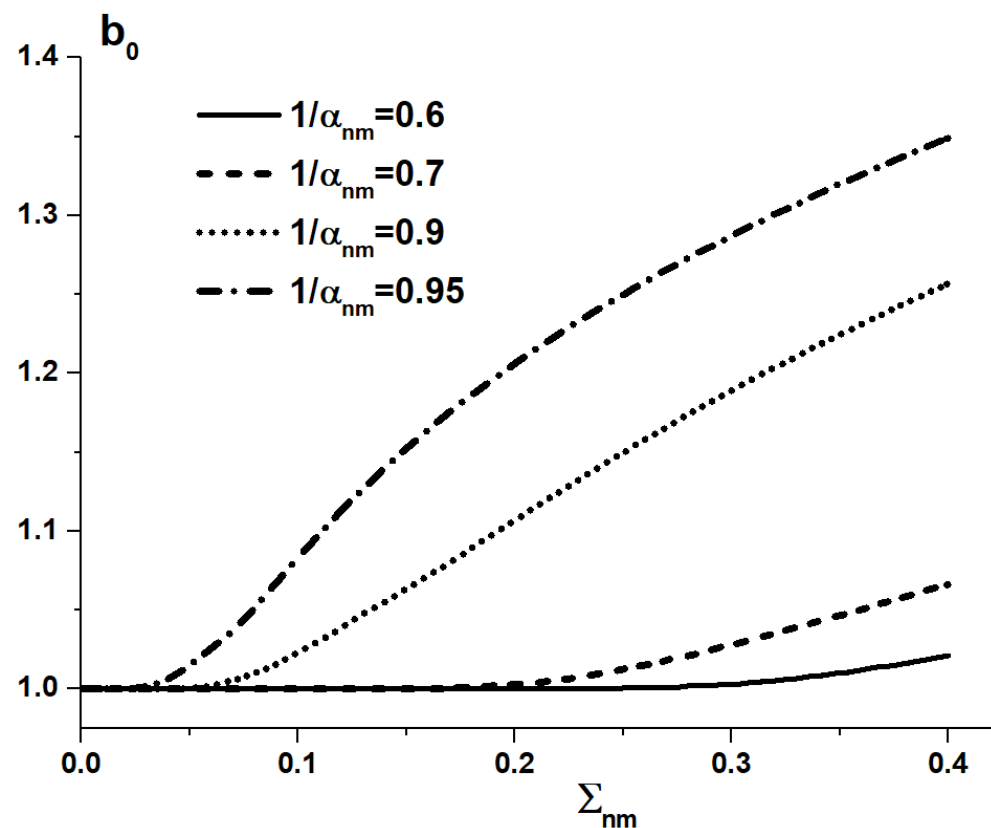


Figure 11. Intensity ratio dependency of the spectral line $b_0 = \frac{\bar{I}_{0r}}{\bar{I}_{0M}}$ on the relative dispersion of the measured intensity Σ_{nm} ; $L = 7$; $K = 3$.

Figure 12 shows the results of a numerical experiment on the application of the proposed algorithm. The frame-by-frame accumulation of the CCD signal was simulated using a random number generator with a probability density defined by Formula (3). The line contours were recorded by the recording system on CCD rulers and reconstructed using the above algorithm for our model problem when $L = 5$; $\Sigma_{0m} = 0.4$; $b_{3m} = 0.95$ and $L = 9$; $\Sigma_{0m} = 0.4$; $b_{5m} = 0.95$. As indicated, the measured and the reconstructed contours have different half-widths if the width at the base is the same. The reasons for this are discussed above. For the central pixel, the effect considered is at its maximum, so the half-width decreases. In this case, the effect for the edge pixels is almost equal to null, which provides the same width at the base of the recorded and the actual contours.

Figure 13 shows the results of experimental application of the proposed algorithm for the case of determining Al in steels for the experimental conditions in Figure 2. From the data in Figure 2, it can be seen that under the selected operating parameters of the SPAS-05 spectrometer (<https://spas05.com/en/products/emission-spectrometers/optical-emission-spectrometer-oes-spas-05-metal-analysis> (accessed on 27 February 2022)), concentrations of several thousandths of a percent are reliably determined. At concentrations less than 1%, the blooming effect is not pronounced. For the relative intensity measured by the traditional method, when the concentration exceeds 1%, the derivative of the dependence $I_{Al}/I_{Fe}(C)$ begins to drop sharply and, at a concentration above 2.2%, the intensity does not depend on the concentration. Thus, the technique for determining the concentration of Al that is described by the calibration curve (Equation (2)) is applicable over the Al concentration range $C = 10^{-3} \div 1\%$. At the same time, the use of the proposed algorithm makes it possible to expand the upper range of its applicability to 2.6%.

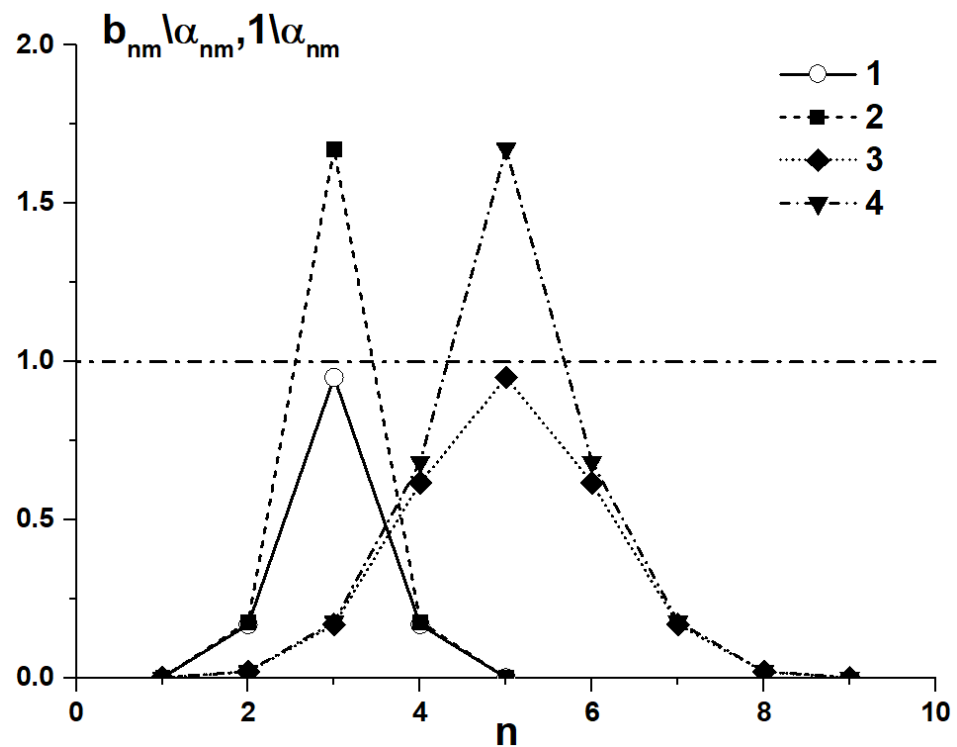


Figure 12. The reconstruction of actual spectral line contour $\frac{\bar{I}_n}{\bar{I}_{max}}$ using the developed algorithm from the measured contour $\frac{\bar{I}_{nm}}{\bar{I}_{max}}$; 1— $\frac{1}{\alpha_{nm}} = \frac{\bar{I}_{nm}}{\bar{I}_{max}}, L = 5$; 2— $\frac{b_{nm}}{\alpha_{nm}} = \frac{\bar{I}_n}{\bar{I}_{max}}, L = 5$; 3— $\frac{1}{\alpha_{nm}} = \frac{\bar{I}_{nm}}{\bar{I}_{max}}, L = 9$; 4— $\frac{b_{nm}}{\alpha_{nm}} = \frac{\bar{I}_n}{\bar{I}_{max}}, L = 9$.

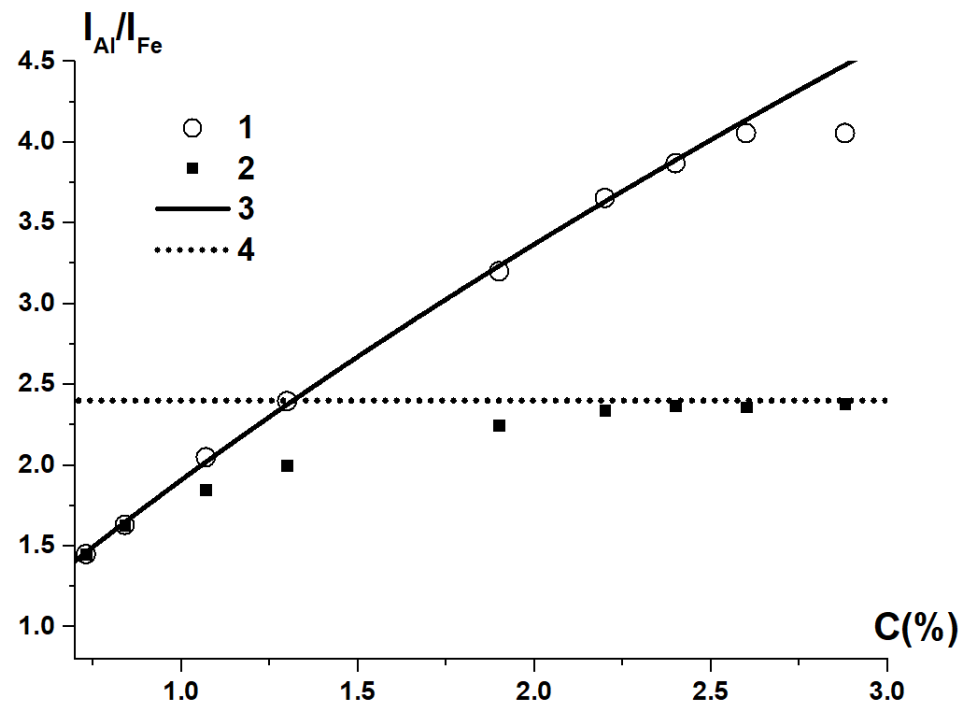


Figure 13. Application of the proposed technique on the example of determining the concentration of Al in steels. The area of high concentrations is shown; the conditions are the same as those in Figure 2; 1—data processing according to the proposed algorithm; 2—data processing according to the traditional algorithm without adjustments for the blooming effect; 3—calibration curve (Formula (2)); 4—limiting relative intensity of the analytical line Al 394.4 nm (reference line Fe 389.57 nm) for the used CCD (TCD1304DG).

5. Conclusions

We conclude by outlining the main results of the study:

- A mathematical algorithm for adjustment of measured analytical line intensities in individual pixels at a CCD upper limit and data processing of the recording system was developed. It can be implemented in the software of modern emission spectrometers.
- The algorithm was tested in a numerical experiment and when determining the concentration of Al in Fe-based alloys.
- It was shown that if relative frame dispersion is significant (20% or more), the adjustment coefficient can reach 2.
- It was clarified that the actual dispersion of analytical line intensities' frame-by-frame distribution can exceed the measured dispersion by one-and-a-half times.
- It was shown that the half-width of the recorded spectral line contour exceeds its real contour.
- All detected patterns were interpreted within the framework of the mathematical algorithm and model.

These results enable us to improve the software for emission spectrometers that use CCDs as recording elements, in order to adjust the calibration curves in the area of high alloying element concentrations. The algorithm can be used not only in emission spectral analysis, but also in any kind of equipment where spectral line intensity is measured with a CCD.

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Appendix A

We calculate value $\bar{I}_{nm}$, using the probability density (Equation (3)). It should be noted that, strictly speaking, value I_{nk} takes discrete values when $k = 1, 2, \dots, M$. In practice, when taking measurements by emission spectrometers, a number of frames M of the order of several hundreds is used. In this case, the relative dispersion value $\Sigma_n = \frac{\sigma_n}{\bar{I}_n}$ does not usually exceed 30–40% (and, as a rule, is significantly lower). Therefore, we can proceed to the limit $M \rightarrow \infty$ and then use a continuous value I_n rather than a discrete one I_{nk} .

Firstly, we calculate the normalization constant A_n . From Correlation (3) we have:

$$A_n \cdot \sqrt{2\sigma_n} \int_{\frac{(I_{nN} - \bar{I}_n)}{\sqrt{2\sigma_n}}}^{\infty} \exp(-x^2) dx = 1.$$

Considering that $I_{nN} \ll \bar{I}_n$ (in practice $\frac{I_{max}}{I_{nN}} \sim 10^3$) and

$$\frac{\bar{I}_n}{\sqrt{2\sigma_n}} \sim \frac{I_{max}}{\sqrt{2\sigma_n}} > 2, \quad (A1)$$

we obtain:

$$A_n = \frac{1}{\sqrt{2\pi}\sigma_n} + O\left\{\exp\left[-\left(\frac{\bar{I}_n}{\sqrt{2}\sigma_n}\right)^2\right]\right\}, \quad (\text{A2})$$

where $\lim_{x \rightarrow 0} \frac{O(x)}{x} = \text{const} < \infty; \text{const} \neq 0$.

If there is an intensity limit, the probability density distribution of the measured values I_{nmk} varies. Indeed, if the actual intensity is $I_{nk} \leq I_{max}$, the distribution I_{nmk} satisfies the correlation (3), and $I_{nmk} = I_{nk}$, but if $I_{nk} > I_{max}$, then $I_{nmk} = I_{max}$. Thus, the probability density of the measured intensity value $P_{nm}(I_{nmk})$ is:

$$P_{nm}(I_{nmk}) = P_n(I_{nmk})\theta(I_{max} - I_{nmk}) + A_{nm}\delta(I_{nmk} - I_{max}), \quad (\text{A3})$$

where $\theta(x) = 0$ if $x < 0$, $\theta(x) = 1$ when $x > 0$; $\delta(x)$ —delta-Dirac function.

According to the definition, if there is a maximum intensity I_{max} , the measured average $\bar{I}_{nm}$ is equal to:

$$\bar{I}_{nm} = \int_{I_{nN}}^{I_{max}} x P_{nm}(x) dx. \quad (\text{A4})$$

If we take $\int_{I_{nN}}^{I_{max}} P_{nm}(x) dx = 1$, for the constant A_{nm} we obtain:

$$A_{nm} = 1 - \int_{I_{nN}}^{I_{max}} P_n(x) dx. \quad (\text{A5})$$

If we take (A1)–(A5) and neglect the second summand in Formula (A2), with the same accuracy as in (A2), we have:

$$\bar{I}_{nm} = \frac{\bar{I}_n}{2} \left[1 + \operatorname{erf}\left(-\frac{I_{max} - \bar{I}_n}{\sqrt{2}\sigma_n}\right) \right] - \frac{\sigma_n}{\bar{I}_n \sqrt{2\pi}} \exp\left[-\left(\frac{I_{max} - \bar{I}_n}{\sqrt{2}\sigma_n}\right)^2\right] + \frac{I_{max}}{2} \left[1 - \operatorname{erf}\left(-\frac{I_{max} - \bar{I}_n}{\sqrt{2}\sigma_n}\right) \right]. \quad (\text{A6})$$

Then we finally obtain the equation linking the measured and actual intensities:

$$b_{nm} \left[1 + \operatorname{erf}\left(-\frac{\alpha_{nm} - b_{nm}}{\sqrt{2}\Sigma_n b_{nm}}\right) \right] - \frac{\Sigma_n \alpha_{nm}}{\sqrt{2\pi}} \exp\left[-\left(\frac{\alpha_{nm} - b_{nm}}{\sqrt{2}\Sigma_n b_{nm}}\right)^2\right] + \alpha_{nm} \left[1 - \operatorname{erf}\left(-\frac{\alpha_{nm} - b_{nm}}{\sqrt{2}\Sigma_n b_{nm}}\right) \right] = 1, \quad (\text{A7})$$

where $\Sigma_n = \frac{\sigma_n}{\bar{I}_n}$ is the relative dispersion of the actual intensity; $\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x \exp(-x^2) dx$;

$b_{nm} = \frac{\bar{I}_n}{\bar{I}_{nm}}$; $b_{nm} \geq 1$; $\alpha_{nm} = \frac{I_{max}}{\bar{I}_{nm}} > 1$.

It necessary to note that the dispersions of the measured and actual intensities σ_{nm}, σ_n , respectively, may vary significantly. This becomes clear from the following considerations. When intensity $\bar{I}_{nm}$ approaches value I_{max} , the selected intensities I_{nk} for the frames (having some index k) may exceed I_{max} . For these frames, the measured values I_{nmk} will be equal to I_{max} , i.e., their distribution does not satisfy Correlation (3) when the dispersion is σ_n . When taking measurements by emission spectrometers based on the dataset I_{nmk} , $k = 1, 2, \dots, M \gg 1$ the dispersion σ_{nm} is calculated using the known formulas. At the same time, Equation (A7) contains the dispersion of the density distribution of the actual intensity probability (Equation (3)). This means that it contains two unknown values $\sigma_n, \bar{I}_n$; to calculate these, we need to find another equation linking the experimentally measured and actual values $\sigma_{nm}, \bar{I}_{nm}$ and $\sigma_n, \bar{I}_n$, respectively.

To do so, we calculate the value σ_{nm}^2 , which is, by definition, equal to:

$$\sigma_{nm}^2 = \int_{I_{nN}}^{I_{max}} (x - \bar{I}_{nm})^2 P_{nm}(x) dx = \int_{I_{nN}}^{I_{max}} (x - \bar{I}_{nm})^2 P_n(x) dx + \left[1 - \int_{I_{nN}}^{I_{max}} P_n(x) dx \right] (I_{max} - \bar{I}_{nm})^2. \quad (\text{A8})$$

By calculating the integrals in Equation (A8), we obtain the correlation we are looking for:

$$\begin{aligned}
 & \int_{I_{nN}}^{I_{max}} (x - \bar{I}_{nm})^2 P_{nm}(x) dx \\
 &= \sigma_n^2 \left[1 - \frac{2}{\sqrt{\pi}} \Gamma\left(\frac{3}{2}, \frac{I_{max} - \bar{I}_n}{\sqrt{2}\sigma_n}\right) \right] - \sqrt{\frac{2}{\pi}} \sigma_n (\bar{I}_n - \bar{I}_{nm}) \exp\left[-\left(\frac{I_{max} - \bar{I}_n}{\sqrt{2}\sigma_n}\right)^2\right] \\
 &+ \frac{(\bar{I}_n - \bar{I}_{nm})^2}{2} \left[1 + \operatorname{erf}\left(-\frac{I_{max} - \bar{I}_n}{\sqrt{2}\sigma_n}\right) \right] \text{ when } I_{max} \geq \bar{I}_n; \\
 & \int_{I_{nN}}^{I_{max}} (x - \bar{I}_{nm})^2 P_{nm}(x) dx \\
 &= \frac{\sigma_n^2}{\sqrt{\pi}} \left[\Gamma\left(\frac{3}{2}, \frac{\bar{I}_n - I_{max}}{\sqrt{2}\sigma_n}\right) \right] - \sqrt{\frac{2}{\pi}} \sigma_n (\bar{I}_n - \bar{I}_{nm}) \exp\left[-\left(\frac{I_{max} - \bar{I}_n}{\sqrt{2}\sigma_n}\right)^2\right] \\
 &+ \frac{(\bar{I}_n - \bar{I}_{nm})^2}{2} \left[1 + \operatorname{erf}\left(-\frac{I_{max} - \bar{I}_n}{\sqrt{2}\sigma_n}\right) \right] \text{ when } I_{max} < \bar{I}_n; \\
 & \left[1 - \int_{I_{nN}}^{I_{max}} P_n(x) dx \right] = \frac{1}{2} \left[1 - \operatorname{erf}\left(-\frac{I_{max} - \bar{I}_n}{\sqrt{2}\sigma_n}\right) \right],
 \end{aligned} \tag{A9}$$

which, together with Equation (A7), gives the system of Equation (5) to calculate the unknown values b_{nm} and Σ_n with the known values α_{nm} and $\Sigma_{nm} = \frac{\sigma_{nm}}{\bar{I}_{nm}}$.

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