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<td>Shinotani, Hisashi</td>
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Visual Spectral Analysis of Steels

by

Hisashi SHINOTANI*

(Received September 10, 1969)

Introduction

Emission spectral analysis takes a leading part in a number of instrumented analyses for metals and alloys because of its speediness and high accuracy.

This analytical method which started with photometric method in the ultra violet region and has developed into photoelectric direct reading method, has made a great contribution to production control in steel making and other any heavy industries. However, this photoelectric instrument is expensive, and is limited in place for its institution.

There are frequent opportunities when one does not expect superior accuracy, but desires only to know the grades of metals and alloys. Visual spectroscope exists for this purpose. However, instruments of this kind are few in number, and far from being prevalent in Japan. (though they are wide spread in Europe and USSR.)

Characteristics of this method are as follows.
1) In general, equipments are inexpensive and small in size.
2) Since analysis is done by the observer’s naked eye, the experimenter can observe temporary variation etc. of the line in detail, and this experiences becomes a superior preliminary knowledge for the operation of Quatometer and Quantovac etc. of more high class photoelectric methods.
3) In qualitative analysis, visual method is most speedy than any other methods.
4) Quantitative analysis also can be done by the use of the rotary polarizer or photometric wedge. Also photometric method are applicable for the visual region as in the UV region.
5) Elements that inradiate spectral line in the visual region cannot be analyzed.
6) Since in both of the quantitative and qualitative analysis, spectral line is radiated into the eye of the observer, obtained results lacks objectivity. (with respect to this weekpoint one can compensate it by the photometric method.)
7) While the equipments of this kind can be operated very easily because of its simplicity, the fact that one can select only one exciting regime and that the slit wides is fixed narrows the range of its use.

The author added improvement in order to put this visual spectroscope to practical use, without any need of great skill, moreover to increase reproducibility and speediness.

As the first step, the author established analytical conditions of carbon steels, low alloying steels and investigated an limitation of its practical use. The details of experiments done are as follows.
1) Making of an atlas of pure iron spectrum in the visual region. (Fig. 2)
2) Qualitative analysis of the alloying elements and impurities in steels.
3) Visual quantitative analysis of the Mn, Mo, Cr, Ni, Cu, V, in plain carbon steels and low alloying steels.

* Department of Mechanical Engineering
Experimental Equipments and Methods

Fig. 1 illustrates the optical design and the exciting circuit of Shimazu Is-30 Matalscope used in these experiments. Light from AC. arc that produced between the specimen laid on the object table and the counter electrode (6 mm φ graphite 120° corn shaped) enters the slit, is condensed by the corimator, separated into the spectrum by two 60° glass prisms, passes through the camera lens and projects on the focus face the picture of emission spectra dispersed in 4000～7000 Å region. This picture can be photographed with the Matalscope-camera attached to this instrument.

Fig. 1. Optical design and exiting source of the experimental equipment.

The author modified this in order to be able to observe a magnified figure of a partial region in the focus screen adapted to Mirax-Laborec camera. (a single lens reflex camera with a transparent focusing screen for the microscope.) Also, the author attached the variable width slit with a shutter for Shimazu QF-60 spectrograph in place of the original simple slit. Experimental conditions employed from the result of a number of preliminary experiments are shown in Table 1.

Known chemical composition standard samples, (various 15 kinds) were used. Shimazu type
Visual Spectral Analysis of Steels

2 micro-photometer was used for quantitative analysis with X-Y recorder.

Table 1. Experimental condition

<table>
<thead>
<tr>
<th>Exciting condition</th>
<th>AC, arc 200 volt 3 amp.</th>
</tr>
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<tbody>
<tr>
<td>Counter electrode</td>
<td>Graphite 6 mm φ 120° corn shape</td>
</tr>
<tr>
<td>Sample shape</td>
<td>Disk</td>
</tr>
<tr>
<td>Analysis gap</td>
<td>2 mm</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Slit width</td>
<td>0.017 mm</td>
<td>0.005 mm</td>
<td>free</td>
</tr>
<tr>
<td>Exposure time and develope</td>
<td>30 sec. ~ 120 sec. 5 min/20° C</td>
<td>——</td>
<td>——</td>
</tr>
<tr>
<td>Eyepiece</td>
<td>Laboratory camera</td>
<td>10 × or 20 ×</td>
<td>20 × 20 ×</td>
</tr>
<tr>
<td>Camera</td>
<td>Laboratory camera</td>
<td>Laboratory camera</td>
<td>Laboratory camera</td>
</tr>
<tr>
<td>Film</td>
<td>Minicopy</td>
<td>Neopan SS</td>
<td>——</td>
</tr>
</tbody>
</table>

Pure Iron Spectrum Atlas and the Qualitative Analysis

The general procedure in qualitative spectral analysis is to determine the wave length of the lines observed and to identify them with the data given in the wave length tables. At present, quartz spectrograph is predominant over others in the spectral analysis and pure iron spectrum called "atlas or map" has been used for this purpose. In visual methods also, atlas of spectrum of this sort is essential for interpreting the spectrum of all metal materials, which is a unique wavelength scale in spectral analysis because the spectrum of iron contains a large number of lines. However, detailed atlas of this sort has not been published.

The author made up this atlas previous to qualitative analysis. The whole region spectrum photographed with Metalloscope camera becomes blurs when enlarged to the size of 10 × or 20 × even with a reduced slit width, and so clear atlas cannot be had with it. The author's atlas illustrated in Fig. 2 were obtained by means of the partial wave-length photo-taking method with the single lens reflex camera as mentioned above. This is the combination picture of 15 pieces of partial region spectrum. Zn, Na, Hg, Cu, V, Mo, W, Cr, Ni, and Mn etc. were used as a basic elements for determining the wave lengths. Fig. 3 shows the linear reciprocal dispersion curve obtained from this atlas. This iron spectrum atlas is the most unique wave length scale not only for the analysis of the iron and steel but also of all other metals and alloys, and such one filled up with wave lengths is essential for spectral analysis. When carrying out qualitative analysis by the means that author devised, one can catch spectral line of the elements in question certainly between two vertical base lines cut on the transparent focusing screen as illustrated in Fig. 4. Therefore it does not require great skill, furthermore one can improve analytical reproducibility. For instance, when one investigates whether Cr may be contained or not, first of all emit the Cr containing certainly standard sample or pure Cr, in the next, after altering the counter electrode, emit a questionable sample, and one will be able to try easily qualitative analysis without dexterities even though he was a beginner. Obtained results are shown at Table 2.
Fig. 2. Pure iron spectrum atlas.
Table 2. Detecting sensibility of the each element.

<table>
<thead>
<tr>
<th>elements and its wave lengths</th>
<th>minimum % of the STD</th>
<th>note</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr 1</td>
<td>5206.04</td>
<td>0.02</td>
</tr>
<tr>
<td>Mo 1</td>
<td>5533.0</td>
<td>0.02</td>
</tr>
<tr>
<td>Mn 1</td>
<td>4823.5</td>
<td>0.08</td>
</tr>
<tr>
<td>V 1</td>
<td>4379.2</td>
<td>0.04</td>
</tr>
<tr>
<td>Ni 1</td>
<td>4714.4</td>
<td>0.59</td>
</tr>
<tr>
<td>Cu 1</td>
<td>5105.5</td>
<td>0.09</td>
</tr>
<tr>
<td>W 1</td>
<td>5053.3</td>
<td>0.85</td>
</tr>
<tr>
<td>Ti 1</td>
<td>4999.3</td>
<td>0.037</td>
</tr>
<tr>
<td>Co 1</td>
<td>4840.3</td>
<td>0.12</td>
</tr>
</tbody>
</table>

Detecting limitations by this means satisfies us and it is beyond the common values of other visual methods.

As stated above, the author felt variations of the analytical difficulty among each element, for instance, in spite of the line itself being indistinct, the line has the superior detecting limitation, or conversely, in spite of the being easily seen clear line, the line has the low detecting sensibility. These factors should be considered as follows. 1) action of a third element. 2) the brightness and the

Fig. 3. Linear reciprocal dispersion curve.
sharpness of the line. 3) disturbance line. Though the personal error by this means can be lowered considerably, if one may apply photographic method, expect more and more superior results. Though the particulars are omitted, the state of V detecting is shown in Fig. 4 as an example. The photographic method gives us evidence and can make good the deficiency of the human eye in short wave-length region.

**Quantitative Analysis (Visual and Photometric Methods)**

The basis of quantitative analysis is based on the assumption that the intensity of the spectral lines from exciting source is proportional to the concentrations of radiated atoms in the sample.

That is; \[ I = AC^n \] \[ \log I = \log A + n \log C \]

where, \( I \); intensity of the spectral line
\( A \); constant, be fixed by exciting condition
\( n \); emission factor too, and takes nearly 1 value by the existence of self absorption, background etc.
\( C \); concentration of the radiated atoms.

The relation curve between \( \log I \) and \( \log C \) shows an incline of \( n \). However, it is impossible to keep invariable exciting conditions, as it is impossible to lead the sample uniformly to the arc column. Therefore the relative intensity comparison between the concentrations of the analysis element and internal standard intensity was done. Until now, homorogous analytical line pairs have been used for the semiquantitative analysis of the visual methods. However, the comparison of the intensities of two spectral lines that lie in separated distances leads to considerable personal error. So the author should give it up. The comparison of intensities the author experimented is the visual method by the eyepiece for visual quantitative analysis with a rotary polarizer, and the photometric method by Laborec camera and micro-photometer. When one uses internal standard, following equations are concluded.

\[ \log I_a/I_s = \log A_a/A_s + na/ns \log C_a/C_s \]

where, \( I_s \); known intensity of the internal standard line
\( I_a \); unknown intensity of the analysis line
\( na, ns \); exciting factor of the internal standard and analysis line respectively
\( C_a, C_s \); the concentration of the internal standard and analysis line respectively.
Since $C_3$ is the constant, equation

$$\log \frac{I_a}{I_s} = \log A + n \log C_a$$

is derived.

In the quantitative analysis, known concentration standard samples have been used, and the calibration curves plotted $\log I_a/I_s$ against $\log C_a$ have been obtained. When the $n=1$, this working curve shows a straight line having the incline of 45° theoretically. The accuracy of the analysis depends a great deal on the selection of the line pairs. Following line pairs have been chosen from the results of preliminary experiments. Fig. 5 shows temporary variation of the intensity of spectral line, as an example for the select of the line pair. Fig. 6 illustrates the optical design of the quanti-

<table>
<thead>
<tr>
<th>Analysis line</th>
<th>Internal standard line</th>
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<tbody>
<tr>
<td>Cr 1 5206.04 Å</td>
<td>Fe 1 5227.19 Å</td>
</tr>
<tr>
<td>Mo 1 5333.05 Å</td>
<td>Fe 1 5501.47 Å</td>
</tr>
<tr>
<td>Mn 1 4823.52 Å</td>
<td>Fe 1 4859.75 Å</td>
</tr>
<tr>
<td>V  1 4379.24 Å</td>
<td>Fe 1 4735.93 Å</td>
</tr>
<tr>
<td>Cu 1 5105.54 Å</td>
<td>Fe 1 5110.41 Å</td>
</tr>
<tr>
<td>Ni 1 4714.42 Å</td>
<td>Fe 1 4710.29 Å</td>
</tr>
</tbody>
</table>

tative eyepiece for Is-30 Metalloscope. The eyefield is divided into the upper and the lower parts by two prisms. When the lever 8 is rotated, the lower prism is turned, the lower eyefield moves from side to side relatively to the upper one. By this, for instance, one can arrange the line of the Fe 1 5227.2 Å comparison line and Cr 1 5206.0 Å analysis line. Moreover, if one desires to equalize the intensities of the upper and lower sides, it can increase (or decrease) the intensities of the upward, decrease (or increase) the downward intensities simultaneously by turning the scale dial 7, rotary polarizer 3 rotates too against the fixed polarizer (two polarizers are combined so that the direction of each absorb axis may be at a right angle to each other), and one can read off $I_a/I_s$ from readings of its indicator.

Fig. 8-1 is the calibration curves be obtained from mean value of five men measuring values (one measuring for one experimenter), and Fig. 8-2 is obtained from the mean value of 25 times measuring of the same experimenter. later shows the upper limit and the lower limit of measuring value too.

![Fig. 5. Temporal variation of line intensity.](image-url)
Hisashi Shinotani

1. upper prism
2. lower prism
3. rotary polarizer
4. fixed polarizer
5. eyepiece
6. auxiliary lens
7. scale dial
8. turning lever of the lower prism
9. view of the eyefield

Fig. 6. Eyepiece for quantitative analysis.

Fig. 7. Visual quantitative analysis of Cr.

This experiment indicates that it is necessary for every experimenter to have his own exclusive calibration curve respectively, still more to carry out analysis while checking it sometimes.

Fig. 8-1. Calibration curves for determination of Mn, Mo. (the mean values of five men, one measuring for one experimenter.)
In order to prevent a mistake of the line pair select, one had better catch a line pair in between vertical two base lines cut in the focusing screen of the Laborec camera likewise in the case of qualitative analysis.

The spectral line intensities can be compared more accurately when the spectroscope has a wide slit, wherefore varying of the slit width the author improved, becomes very useful. But when the slit width is too wide, adjoining lines may overlap, in addition, the background is increased noticeably.

Then the maximum permissible slit width should be chosen.

Though the visual method might be equal to the photoelectric method in its quickness and readiness, we cannot be satisfied with the accuracy because of the momentary unstability of the line intensity and the differences of spectral sensibility of each person. Then the author applied the photometric method, and checked up on the exact homologous intensity of man's sight objectively. Still more, in the photometric method line intensities are averaged because the integrated intensities are shown, conversely in the visual method, intensity is measured momentarily. The same equipment and conditions with visual measurement are used in this photometric method (but the 20 × ordinaly eyepiece is used instead of the quantitative eyepiece). In the case of the photometric method, it is necessary to investigate the photo emulsion. The relation between the density of blackness of the photo emulsion and the log exposure time or the log concentration of the element is

\[ D = \tau \log I + \gamma \rho \log t + \gamma \log l/a \]

therefore

\[ Da = \tau \log Ia + \gamma \rho \log t + \gamma \log l/a \]
\[ Ds = \tau \log Is + \gamma \rho \log t + \gamma \log l/a \]

where, \( Da, Ds \); the density of darkness of the analysis line and of the internal standard line respectively,

\( \tau \); contrast, incline (\( \tan \theta \)) of the proportional region of the characteristic curve

\( \rho \); the Shawarzshild index

\( t \); the exposure time

\( a \); the emulsion inertia

\( Ia, Is \); the intensity of the analysis line and of the comparison standard line respectively.
Difference of the density of blackness between the analysis line and the internal standard line, $\Delta D$ is

$$\Delta D = D_a - D_s = \gamma \log I_a/I_s.$$  

While, between $C_a$ and $I_a$, $I_s$ on the assumption that the exciting condition is constant

$$\log I_a/I_s = \log A + n \log C_a.$$ 

therefore,

$$\Delta D = \gamma \log A + \gamma n \log C_a.$$  

When $n = 1$,

$$\Delta D = \gamma \log A + \gamma \log C_a.$$ 

Since $\gamma$, $A$ is a constant as in the case of the same emulsions, under the same exciting conditions, and $n$ is also constant in the case of identical analysis sample $D$ becomes proportional to $\log C_a$, and they were arranged in linear relation. Since $C_a$ varies with known concentrations in the above equation, if one measures $\Delta D$ against $C_a$, $\gamma$, $A$ is determined. $D_a$, $D_s$ keeps linear relationship with $\log I_a$, $I_s$ only in the linear region in the Hurter-Drifield characteristic curve. The author chose Table 1 photo-taking conditions from above considerations and preliminary experimental results. Photographed films were laid on the microphotometer, and $I_{alls}$ were obtained from readings of the X-Y recorder, then the acquired calibration curves illustrate in Fig. 9.

![Figure 9. Calibration curves for Mn and Cr.](image)

Coefficient of variation of each element that shows the reliability of the analytical values by this means was calculated by the following equation.

$$v = 100 / \sqrt{\sum d^2 / n - 1}$$

where, $v$ ; modulus of mean deviation  
$\epsilon$ ; mean value of arithmetical sum  
$n$ ; repeated experimental times  
$d$ ; the deviation of the obtained analytical value contrary to $C$.

Then obtained results were shown in Table 4.
Table 4. Accuracy of the photometric method

<table>
<thead>
<tr>
<th>Elements</th>
<th>Chemical analysis value</th>
<th>modulus of mean deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>0.62%</td>
<td>16.8%</td>
</tr>
<tr>
<td>Mo</td>
<td>0.52%</td>
<td>15.0%</td>
</tr>
<tr>
<td>Mn</td>
<td>0.83%</td>
<td>10.4%</td>
</tr>
<tr>
<td>V</td>
<td>0.94%</td>
<td>11.9%</td>
</tr>
<tr>
<td>Cu</td>
<td>0.25%</td>
<td>14.5%</td>
</tr>
<tr>
<td>Ni</td>
<td>0.80%</td>
<td>28.5%</td>
</tr>
</tbody>
</table>

Conclusion

As the first step of the study in the emission spectral analysis in visual region that, at present, seems to be despised and disregarded in our country, the author has made a detailed pure iron spectrum atlas and facilitated prospective studies. In the qualitative analysis the author devised observing means that extends the merit of the visual qualitative analysis and by which one can expect the highest detecting sensitivity.

For the quantitative visual analysis the author substituted the variable width slit for the original slit, by which devices, one can easily analyze since the slit width can be chosen freely. Because the ocular spectral sensitivity is inferior to that of the photo emulsion, and in order to apply integrated intensities, the author tried the photometric method.

As a results, satisfying results were obtained.

In the future, author will examine the materials and shapes of the counter electrode, exciting generator, etc. and continue to study the application for the analysis of other metals and alloys.

Acknowledgement

The author wishes to express his gratitude for the advices received from Dr. Hamaguchi, and Mr. T. Yoshinaka. (a member of the Industrial Research Institute, Osaka Pref.) Also acknowledgement is due to Mr. T. Ishida. and Mr. M. Tsunai. for their help with the experiments.

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