RECENT DEVELOPMENTS IN JAPANESE
SPECTROSCOPIC INSTRUMENTS

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Recently, spectroscopic instruments have been important not only in pure
researches but in industry in Japan as in other countries. There were three
manufacturers of spectroscopic instruments, but many new ones have ap-
peared and are producing a variety of spectroscopic instruments at present.
Perhaps almost all types of spectroscopic instruments made in the world
are produced in Japan and the number of spectroscopic instruments ex-
ported has been increasing.

Typical spectroscopic instruments produced will be enumerated and
researches on instruments or their parts will be explained.

SPECTROSCOPIC INSTRUMENTS FOR EMISSION SPECTRA

Spectrographs with a quartz prism are still being used widely in the metal
industry. Shimadzu Seisakusho Ltd. has been the only manufacturer of such
spectrographs in Japan. Figure 1 shows the picture of one of the quartz
spectrographs of Littrow mounting. As grating instruments the company is
manufacturing spectrographs of Ebert mounting \((f = 3.4 \text{ m})\), and vacuum
concave grating spectrographs which are available for photoelectric measure-
ments. Figure 2 shows the optical layout of one of the vacuum spectrographs.
The instruments for photoelectric quantitative emission spectral analysis,
on which researches were made by the author et al.\(^1\) originally, have been
developed into instruments of a direct reading or an automatic recording type

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Figure 1. Quartz spectrograph with Littrow mounting
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Figure 2. Optical layout of a vacuum spectrograph which has a 2m concave grating and many photoelectric detectors

- $L$: Spark stand
- $P$: Protector
- $Q$: Lens
- $M, m$: Mirror
- $R$: Reflected beam
- $G$: Focal curve
- $D_1, D_2$: Photomultiplier
- $S$: Slit

with a grating spectrograph by the company. Figure 3 shows one such instrument for spectrochemical analysis. Moreover, research in which the output of the photomultiplier is treated digitally and the correction of the working curve of the spectrochemical analysis is calculated automatically has been completed by Minami et al. The principle of the digital operation is shown in Figure 4.

Figure 3. Instrument for photoelectric spectrochemical analysis

Research on ruling engines for gratings has been carried out in Japan for many years. Hitachi Central Research Laboratories and the Institute for Optical Research of Tokyo University of Education will finish their ruling engines in the near future. Most gratings used in these instruments were imported from the U.S.A.

Regarding concave grating mountings, Seya and Namioka developed a new mounting, the so-called "Seya Mounting", which satisfied the conditions required for a concave grating to be used in photoelectric spectrometric work. They used Beutler's light pass function and got an approximate solution to fulfill the conditions. The concave grating is rotated around the axis that passes through the vertex of the grating, and is parallel to the grooves of the grating, and the angle between the incident and emergent rays must
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Figure 4. Block diagram of digitally calculating circuit for the correction of working curves

be fixed at about 70 degrees. As a result, the angle of incidence and diffraction becomes comparatively large, and, therefore, the astigmatism is also large. The Seya mounting has been used in many concave grating spectrometers, especially those for the ultraviolet range in Japan and foreign countries. Figures 5 and 6 show the layout of the optical system and the

Figure 5. Optical layout of a vacuum spectrometer with a Seya mounting

SP: Pump for light source
S₁: Entrance slit
SD: Slit drive
V: Gate valve
B: Light baffle
F: Flange to which the camera part is to be attached

G: Concave grating
T: Grating table
P: Pump
SS: Scanning mechanism
VS: Vacuum seal
V: Slit
S₂: Exit slit
C: Cryostat
PM: Photomultiplier

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picture of the vacuum spectrometer of the Seya mounting constructed in Kyoto University. Onaka\textsuperscript{4} devised a mounting locating the axis of rotation at a point away from the grating vertex. Miyake and Katayama\textsuperscript{5} provided more exact solutions and introduced a concave grating mounting, including the Seya mounting and a mounting in which the concave grating was translated in a certain direction.

**RAMAN SPECTROMETER**

Shimomura \textit{et al.}\textsuperscript{6} have completed a Raman spectrometer of photoelectric recording type with a plane grating. To make more energy available, a double pass system with a plane mirror is used. The image of a spectral line curves in general with a straight entrance slit, and the curvature of the image is different according to wavelength. In their mounting, the curvature is cancelled by a double pass system. If the entrance slit is straight, the images of all spectral lines become straight. This device increases the resolution of the spectrometer and makes the construction of the slits easier. This Raman spectrometer has other excellent features and has been manufactured by Shimadzu. \textit{Figures 7 and 8} show the layout of the optical system and the picture of this spectrometer.

**SPECTROSCOPIC INSTRUMENTS FOR ABSORPTION SPECTRA IN THE VISIBLE AND ULTRAVIOLET REGION**

Many spectrophotometers incorporating a direct reading Littrow mounting with a glass or a quartz prism have been manufactured by Shimadzu, Hitachi Ltd., Tokyo Koden Ltd. and other manufacturers, and have been
Figure 7. Optical layout (vertical section) of a Raman spectrometer

- **T**: Raman tube
- **L₁, L₂, L₃, L₄**: Condenser lens
- **S₁**: Entrance slit
- **M₁**: Collimator
- **M₂, M₃, M₄**: Plane mirror
- **IS**: Image slit

Figure 8. The spectrometer illustrated in Figure 7

used in various fields, for example in industry, and biological and medical research. Automatic recording spectrophotometers for the same purpose have been manufactured in recent years by Hitachi and Shimadzu. Those instruments adopt the usual measuring system of “electric direct ratio”. Figure 9 shows the Hitachi instrument of this type.
Figure 9. Automatic recording Spectrophotometer for absorption spectra

Figure 10. A filter spectrophotometer
Simpler, easier to handle, and less expensive spectrophotometers than those described above are in great demand in many fields. Filter photometers are suitable for such purposes. Interference filters between Ag films separated by an MgF₂ film have been studied by the author et al.⁷ and have been developed by Hitachi, Tokyo Shibaura Electric Co., Ltd. (TSE) and Vacuum Optics Corp. of Japan for several years. Any monochromatic filter in the region from 370 to 750 mμ, of which the maximum transmission is about 25–40 per cent and the width of pass band is 10–20 mμ depending on the wavelength region and the demand in spectrophotometers, are manufactured. In general, such a filter is stuck on a glass filter to cut short wave radiation of higher orders and to protect films. The cost of filters is much cheaper than that in other countries. This is the reason why so many filter photometers have been manufactured by several manufacturers, among which some use a photocell and others use a phototube. Figure 10 shows the picture of one such spectrometer.

For these spectrophotometers, phototubes which have a high sensitivity in a wide wavelength region of the visible and ultraviolet are desirable so as to make unnecessary the use of two kinds of phototubes to cover this wide region. Sugawara⁸ investigated a wide range phototube, of which the cathode is ordinary silver caesium oxide photo-cathode and the window is evaporated with a semi-transparent antimony–caesium (or bismuth–caesium) film. This window has a transparency of 50–90 per cent in the range 700–800 mμ, as shown in Figure 11, and has a high sensitivity for radiation below 600 mμ. Figure 12 shows the sensitivity of this phototube compared with that of an ordinary antimony–caesium and silver caesium oxide phototubes. Such phototubes are usable in the spectral region from 200 to 1000 mμ if

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*Figure 11. Transmittance of the window of the phototube*
the envelope is made of fused silica instead of glass, and they have other good features (no trouble with non-linearity of photocurrent and no fatigue effect) which help in the measurement of very weak radiation as in a spectrophotometer. These phototubes have been manufactured by Hitachi. Satisfactory photomultipliers which have high sensitivity even in the 200 μm region have been manufactured by Hamamatsu Television Co., Ltd.

Recently, the so-called "atomic absorption photometer" has been used in spectrochemical analysis. In such analysis the profile of absorption lines has an influence upon the accuracy of analysis. Shimazu et al. measured the profile of spectral lines from the exciting flame through a prism monochromator and a Fabry–Perot interferometer as shown in Figure 13. The

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**Figure 12.** Photosensitivity of the phototube

- **a:** Photosensitivity of the phototube
- **b:** Photosensitivity of the silver caesium oxide phototube
- **c:** Photosensitivity of the antimony-caesium phototube

**Figure 13.** Block diagram of the interferometric spectrometer for measuring the profile of spectral lines
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profile is recorded by making the wavelength scanning by changing the air pressure in the interferometer. Figure 14 shows the profile of the sodium-D line at various concentrations. The profile depends upon the effects due to several kinds of broadening of spectral lines, and the self-absorption gives the

![Graph showing profile of sodium-D line at various concentrations](image)

*Figure 14.* Profile of sodium-D line at various concentrations

most important influence upon the linearity of working curves in spectrochemical analysis as shown in Figure 15. Hitachi are producing several kinds of hollow cathode lamps, such as Ca-, Mg-, Al-, Fe-lamps which emit sharp resonance lines of these elements, as the source of atomic absorption spectrometers.

![Graph showing working curves in spectrochemical analysis](image)

*Figure 15.* Working curves in spectrochemical analysis

- $N_2$: Relative self-absorption in the light source
- $N_3$: Relative concentration
- Real line: Total absorption method
- Broken line: Peak absorption method
Miyata et al.\textsuperscript{10} investigated a reflecting microscope objective and microspectrophotometers have been manufactured by Olympus Kogaku-Kogyo Co. Ltd. Figure 16 shows the optical layout of the instrument. The radiation from a tungsten filament lamp, hydrogen lamp, or high pressure mercury lamp is fed to a Littrow-type double monochromator with quartz prisms. Monochromatic radiation from the exit slit of this spectrometer enters the microscope which has a reflective objective. A photomultiplier or a lead sulphide cell is used as a detector. Spectrophotometric measurements in the region from 2 $\mu$ to 240 $\mu\mu$ are possible with samples as small as about 1 $\mu$ or with samples of 0.0001 cm$^3$ with a micro cell. The instrument is of course

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{optical_layout}
\caption{Optical layout of a microspectrophotometer}
\end{figure}

<table>
<thead>
<tr>
<th>HG, W:</th>
<th>Light source</th>
</tr>
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<tbody>
<tr>
<td>S$_0$, S$_d$, S$_f$:</td>
<td>Slit</td>
</tr>
<tr>
<td>P:</td>
<td>Prism</td>
</tr>
<tr>
<td>L:</td>
<td>Lens</td>
</tr>
<tr>
<td>SL:</td>
<td>Slit lens</td>
</tr>
<tr>
<td>H:</td>
<td>Pin hole</td>
</tr>
<tr>
<td>HM:</td>
<td>Half-mirror</td>
</tr>
<tr>
<td>RS:</td>
<td>Ring slit</td>
</tr>
<tr>
<td>SS:</td>
<td>Sample stage</td>
</tr>
<tr>
<td>C:</td>
<td>Condenser</td>
</tr>
<tr>
<td>Ob:</td>
<td>Objective</td>
</tr>
<tr>
<td>PP:</td>
<td>Phase plate</td>
</tr>
<tr>
<td>Oc:</td>
<td>Ocular</td>
</tr>
<tr>
<td>AC:</td>
<td>Absorption cell</td>
</tr>
<tr>
<td>F:</td>
<td>Film</td>
</tr>
<tr>
<td>D:</td>
<td>Diaphragm</td>
</tr>
<tr>
<td>V:</td>
<td>Viewer</td>
</tr>
<tr>
<td>PbS:</td>
<td>Lead sulphide cell</td>
</tr>
<tr>
<td>PM:</td>
<td>Photomultiplier</td>
</tr>
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</table>
available as a spectrophotometer and a microscope (even phase-contrast type). Figure 17 shows the picture of the instrument.

**COLOUR SPECTROPHOTOMETER**

A few spectrometers for colour measurements have been produced. The calculation of tristimulus values from spectral curves is troublesome. Azuma et al.\textsuperscript{11} developed a new "Colour Computer", which combines a recording spectrophotometer with a digital tristimulus integrator. A motor driven double Littrow monochromator scans the region from 760 to 380 m\(\mu\), while an electrical servo system keeps the wavelength width of the slit constant. Behind the exit slit of the monochromator is a rotating 180° mirror sector set at 45° to the beam. Half the time this mirror reflects the beam against another 45° mirror producing a displaced beam parallel to the original. Alternatively, at 25 c/s these beams illuminate a reflecting sample and a reference standard. A photomultiplier tube picks up the light reflected from the sample and from the standard at 45° and drives a photometric
Figure 18. Comb of "Colour Computer"

Figure 19. "Colour Computer"
comb inserted in the standard light beam. On the inner surface of the arc-shaped photometric comb are 250 mirror facets as shown in Figure 18. A hexagonal mirror sweeps light beams across the facets at a 150 c/s repetition rate. The light reflected from these facets is interrupted at a 50 kc rate by the spaces between them, so the photomultiplier receives repeating 50 kc pulse groups whose number of pulses is proportional to the spectrophotometric value. Colorimetric integration is based on a modified selected ordinate method with supplementary ordinates. Spectral reflectances or transmittances at \( n \) selected ordinates are multiplied by an appropriate coefficient of \((1/2)^n\) and summed. The selected ordinates and coefficients are such that the summations give the value of \( X, Y \) and \( S \) \((= X + Y + Z)\) directly. The selected ordinate signal generator consists of a 35 mm film driven by the wavelength drive motor, a projector and a receiver head. This generator provides the position signal and the category \((X, Y, S\) and the appropriate coefficient of \((1/2)^n\) signal of the selected ordinate. Each of the integrating circuits for \( X, Y \) and \( S \) is a five-digit decimal counter. When the spectrophotometric curve is completed in two minutes, the counter displays the values of \( X, Y \) and \( S \) immediately. Figure 19 shows the picture of the instrument and Table 1 gives an example of the results obtained with

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mean</th>
<th>Standard deviation</th>
<th>Maximum deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( X )</td>
<td>0.41814</td>
<td>±0.00006</td>
</tr>
<tr>
<td></td>
<td>( Y )</td>
<td>0.40047</td>
<td>±0.00008</td>
</tr>
<tr>
<td></td>
<td>( S )</td>
<td>1.75986</td>
<td>±0.00034</td>
</tr>
<tr>
<td></td>
<td>( x )</td>
<td>0.23760</td>
<td>±0.00006</td>
</tr>
<tr>
<td></td>
<td>( y )</td>
<td>0.22756</td>
<td>±0.00006</td>
</tr>
<tr>
<td></td>
<td>( X )</td>
<td>0.47726</td>
<td>±0.00013</td>
</tr>
<tr>
<td></td>
<td>( Y )</td>
<td>0.53672</td>
<td>±0.00020</td>
</tr>
<tr>
<td></td>
<td>( S )</td>
<td>1.73290</td>
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<tr>
<td></td>
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<td>0.27541</td>
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<tr>
<td></td>
<td>( y )</td>
<td>0.30972</td>
<td>±0.00012</td>
</tr>
</tbody>
</table>

the instrument. Repeated measurements of small colour differences prove that the computer can discriminate between about 100 million surface colours. This instrument will be manufactured by TSE very soon.

**SPECTROSCOPIC INSTRUMENTS IN THE INFRA-RED REGION**

Infra-red prism spectrometers have been developed in Japan for about ten years. Japan Spectroscopic Co. Ltd. (JS), Hitachi, and Shimadzu have produced a great number of such spectrometers. All instruments have been of the double beam optical null type, and the Hitachi instrument has a microscope as an attachment as shown in Figure 20.

Kudo\(^{12}\) constructed \((a)\) a double-beam double-pass spectrometer, \((b)\) a

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Figure 20. Microscope attached to an infrared spectrometer

Figure 21. Optical layout of a double-beam double-pass spectrometer

- **LS**: Light source
- **M**: Mirror
- **C**: Absorption cell
- **S**: Slit
- **P**: Prism
- **TC**: Thermocouple

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double-beam triple-pass spectrometer, (c) a double-beam spectrometer with double monochromators in which each is of the single-pass type, (d) a double-beam double-pass spectrometer with double monochromators in which the first is of the single-pass and the second is of the double-pass type. In these spectrometers, the Walsh-type chopper was not used because a chopper to make a double-beam was necessary. Kudo compared the resolution, scanning speed and false radiation obtained experimentally with theoretical values. For increasing the resolution and shortening the recording time, any of the above type of spectrometers can be used, but the double-beam double-pass spectrometer has proved to be the most practical spectrometer. Figures 21 and 22 show the layout of the optical system and the picture of the instrument.

The author et al.\textsuperscript{13} obtained the geometrical aberrations of the optical system used in an ordinary infrared prism or grating spectrometers by a ray tracing method. The effect of aberrations on the resolution is much less than that due to diffraction. This result indicates that one can expect the development of faster instruments if it is possible to obtain excellent mirrors, prisms and gratings.

For some measurements, simpler, more compact and less expensive infrared spectrometers are preferable. The three manufacturers mentioned above are producing such spectrometers with an air-tight system which can be used without trouble in a room of high humidity.

To increase the resolution, spectrometers which use a fore-prism and a main dispersing grating have been developed by these three manufacturers.
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*Figure* 23 shows the picture of a spectrometer of this type by Shimadzu, and *Figure* 24 a new design of grating holders and cams. The device enables many gratings to be mounted in one instrument.

*Figure* 23. A grating infrared spectrometer

*Figure* 24. Grating holders and cams
Figure 25. Optical layout of a far infrared spectrometer

L: Light source  T: Transmission filter
M: Mirror  S: Slit
R: Reststrahlen holder  G: Grating holder
F: Scatter plate  D: Golay cell
CH: Chopper

Figure 26. The spectrometer illustrated in Figure 25
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Some infra-red spectrometers for special purposes, for example, to analyse the concentration of heavy water, have been constructed by Hitachi.

Most kinds of synthetic crystals used in infrared spectrometers are produced by Horiba Instruments Inc., JP and Shimadzu. Thermopiles and lead sulphide cells of high quality have been produced by several manufacturers.

A far infrared spectrometer was constructed by the author et al., and researches on instrumentation in the far infrared region were conducted. These led to the development of special components, for example, a polarizer with a polyethylene sheet pile and transmission filters of polyethylene sheet containing powder of reststrahlen crystals. Commercial far infrared spectrometers will be manufactured in Hitachi and JS in the near future. Figures 25 and 26 show the optical layout (optical null system) and the picture of the prototype model of such a spectrometer made by Hitachi. A spectrum of water vapour absorption in the region from 270 to 80 cm\(^{-1}\) obtained by double-beam operation is shown in Figure 27. The resolution of two pairs of lines with a separation of 0.87 cm\(^{-1}\) and 0.52 cm\(^{-1}\) respectively is shown in Figure 29.

Gain: 0.83 Time const: 15 sec Scan. rate: 0.84 cm\(^{-1}\)/min

![Diagram of spectrometer](image)

\[ S = 1.3 \quad S = 1.4 \quad S = 2.2 \quad S = 3.5 \quad S = 1.5 \quad S = 2.0 \quad S = 2.5 \text{mm} \]

*Figure 27.* Spectrum of water vapour; reststrahlen crystal, grating constant and slit width are shown below the spectrum; the curves in the region of 260 and 240 cm\(^{-1}\) show the interference effect of polyethylene windows of the absorption cell; the overlapping range can be seen in the region of 235 and 125 cm\(^{-1}\)
The optical layout and the picture of the infrared gas analyser manufactured by Horiba are shown in Figures 29 and 30.

Regarding interferometric spectrometers, Yashima et al.\textsuperscript{17} reported preliminary experiments in the visible region, and Mizojiri Seisakusho Ltd. is producing interferometric instruments. A far infrared interferometric spectrometer, which consists of an interferometer of the Michelson type and a special electronic computer, is under construction in the author's laboratory. The spectrogram will be translated from the interferogram and recorded automatically with the instrument.

References
3. M. Seya. Sci. of Light (Tokyo) 2, 8 (1952);
   Private communication.
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11 B. Shimazu and A. Hashimoto. Private communication.