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电感耦合等离子体发射光谱的光谱仪

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Spectrometers for ICP-AES*

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The spectrometer is a very important integrant of an ICP-AES system. In this talk, the general architecture and requirements of the spectrometer for ICP-AES, the grating, the simultaneous multichannel and sequential spectrometers, *etc.*, will be reviewed.

1. Requirement of Spectrometers for ICP-AES

The function of the spectrometer in an ICP-AES system is: (1) to disperse the radiation from the ICP by wavelength into a spectrum and to isolate the analyte line(s) by exit slit(s), and (2) to measure the intensities of the isolated lines so that they can be converted into concentration of the analytes in the sample. According to the characteristics of the ICP source, principal requirements of the spectrometer are as follows:

1. A wavelength coverage of around 170-800nm is preferable, to include the most sensitive ICP lines of all the detectable elements.
2. Vacuum (preferable) or Ar purged optics for wavelengths below 200nm.
3. Bandpass of at least 0.03nm in UV to minimize spectral interferences.
4. Least stray light by proper design and choice of components for the spectrometer.
5. Mechanical stability and minimal (or compensated) temperature effect.
6. Measuring system should match the 10^1-10^6 dynamic range of the ICP.

2. Grating Spectrometers

A spectrometer has the following major components: The characteristic radiation of the sample emitted from the excitation source is focused on the entrance (primary) slit of the spectrome-

* Transcript of an Invited Lecture presented at the Training Course on Atomic Spectroscopy, Fifth Asian Chemical Congress, Kuala Lumpur, November, 1993.

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ter, here a disperser (a grating or prism) separates the radiation into its analytical spectrum and an imaging (focusing) optics forms the monochromatic images of the entrance slit (the spectral lines) on a focal plane, on which exit (secondary) slit (s) is (are) placed to isolate the line(s) to be measured by the detector (s), *i. e.* photomutlipliers (PMTs) placed behind the exit slit (s). The grating spectrometers are most popular for ICP-AES. Numerous reviews on this subject have been published (*e. g.* [1,2]). Fig. 1[3] shows the schematic diagram of a typical multichannel grating spectrometer.

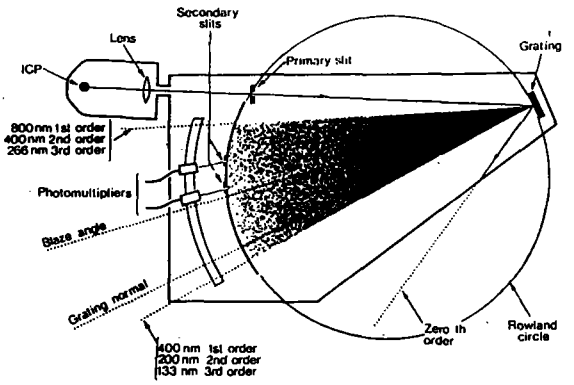

Figure 1. Scale diagram of the optics of a polychromator system in the Paschen-Runge mounting with the grating blazed for maximum reflection of 600 nm in the first order.

2. 1. The Diffraction Grating

The Diffraction Grating is a series of a large number of narrow, straight, parallel and equally spaced grooves (typically 1200 to 3600 gr/mm) in a reflecting material, capable to disperse light into a spectrum. In modern gratings the grooves are either mechanically ruled or holographically recorded on a plane or concave aluminum coated ceramic substrate of very small coefficient of expansion. The groove density (number of grooves per mm) is an important parameter of the grating. With other conditions fixed, the higher the groove density, the higher the resolving power. Plane gratings are used in most sequential instruments (monochromators), and concave gratings in most simultaneous instruments (polychromators).

Ruled and holographic gratings. Ruled gratings, if blazed at a suitable angle, can provide high intensity spectra in the second and third orders, thus providing very wide wavelength coverage. For example, the spectrometer shown Fig. 1, with a ruled grating blazed at 600 nm, gives intense spectra in the first, second and third orders for different wavelength ranges as shown in the figure, providing for simultaneous determinations using visible lines for the alkali metals, the UV lines for most elements and the vacuum UV lines for S, P, C *etc.* This entire wavelength range can not be provided by spectrometers with a single holographic grating, even a " blazed" one, as the second- and third-order spectra have much lower intensities. Interferometrically controlled ruled gratings have spectral " ghosts" and stray lights somewhat stronger than those of the holographic, but are still too weak to be troublesome in normal ICP practice.

2. 2. Polychromator

Most polychromators are based on the Pachen-Runge mounting, where the concave grating has the combined function of dispersing and focusing (imaging), and the entrance slit, the grating and the exit slits lie on the "Rowland circle", with the grating tangential to this circle, which diameter

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equals to the radius of curvature of the concave grating. The Pachen-Runge mounting provides the greatest wavelength coverage and is especially suitable for polychromators, of multichannel spectrometers, as many slits can be placed along the Rowland circle (Fig. 1). This implies that it can determine many elements at a time.

The entrance slit in many polychromators can be moved manually or under computer control along the circle allowing small portions of the spectrum to be scanned.

A polychromator should have good mechanical and thermal stability to ensure perfect alignment of the exit slits. The optical cell should be rigid and shock-mounted. To minimize temperature effect, some instruments employ internal thermostatic control at a temperature higher than the room temperature, say, 30±0.5℃, while some manufacturers carefully select components having the same very small expansion coefficient for use in the optical cell and use fused quartz for the grating substrate, and get good stability without internal thermal control.

2. 2. 1. **Exit Slits.** An individual channel in a polychromator consists of the exit silt, sometimes a condenser mirror, a PMT, and the electronics for integrating, amplifying and outputting the signal. The slits can be simply engraved accurately into a thin metal strip or several strips, such slits are not adjustable but easier to align. Some instruments have more than 260 prealigned slits engraved in the strips, with unwanted ones covered and can be easily uncovered for later needs. Alternatively, slits may be separate devices supported by frames much wider than the slits, and mounted individually along the Rowland circle, each slit can be finely adjusted for wavelength, only with considerable skill and time, but any two slits cannot be closer than the width of the frame. In either case, slits cannot be added, removed or adjusted without shutting down the instrument and opening the optical cell, and a qualified engineer.

2. 2. 2. **The " n+1" and " n+m" systems.** The inflexibility of a polychromator system can be remedied to some extent by providing a monochromator which looks the ICP at the same time as the main spectrometer. With its electronics coupled to the main instrument, it can serve as an additional variable-wavelength channel, the so-called" n+1 channel". It is useful for investigative spectral scans for a certain element. If a sequential spectrometer is coupled to the polychrometer, the complex is called an " n+m" system, and is expensive, too. Schematic diagram of a polychromator with the " n+1" is shown in Fig. 2.

2. 2. 3. **Vacuum vs. Ar Purged Optic.** The spectral range of 170-200mm contains useful lines for a number of elements, exp. for C, P, and S. It is essential to employ a vacuum or Ar purged spectrometer for measurements in this region. With a well-designed low-volume optical cell," demand-only" pumping of 5% duty cycle with a small vacuum pump system is sufficient. If Ar purging is employed, the Ar should have a purity of higher than 99. 999% for satisfactory results.

2. 3. **Sequential Monochromator**

A monochromator with a computer controlled wavelength drive can be used to determine elements sequentially by ICP-AES. The Czerny-Turner mounting with a plane grating is most widely used for the spectrometer (Fig. 3). It has only one exit slit and can be used to determine as many elements as you want to one by one.

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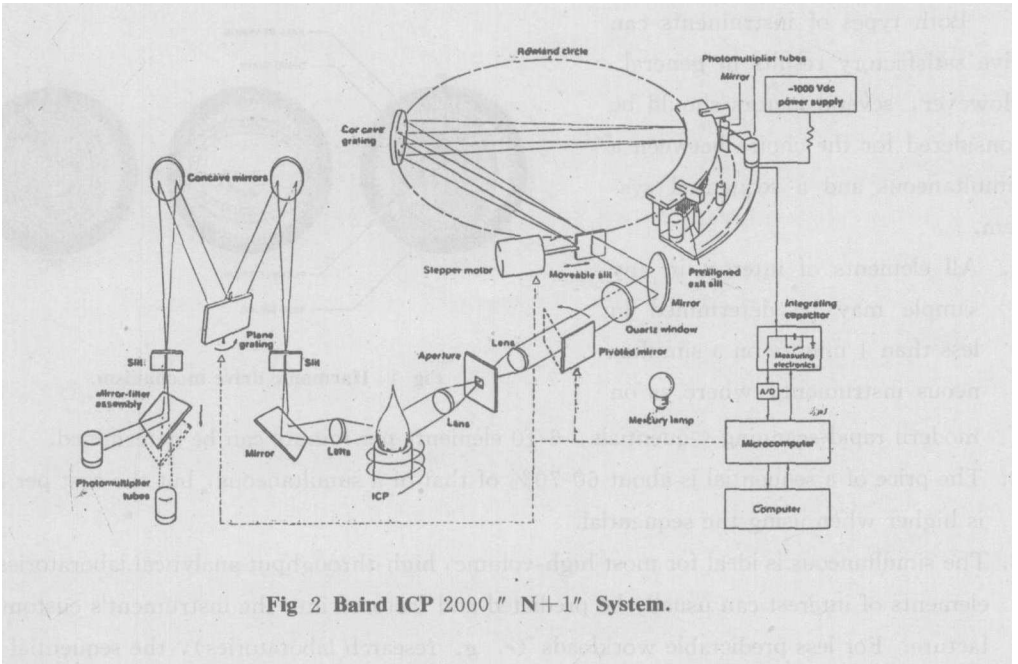

Fig 2 Baird ICP 2000″ N+1″ System.

The mechanism for rotating the grating in minute steps to bring the required wavelengths to the exit slit in most sequential spectrometers is a gear reduction system driven by a stepper motor. Several gear reduction stages are necessary to produce the required reduction, and each stage introduces imprecision, which is then amplified by the subsequent stage. The low degree of tooth engagement on the gears results in backlash problem.

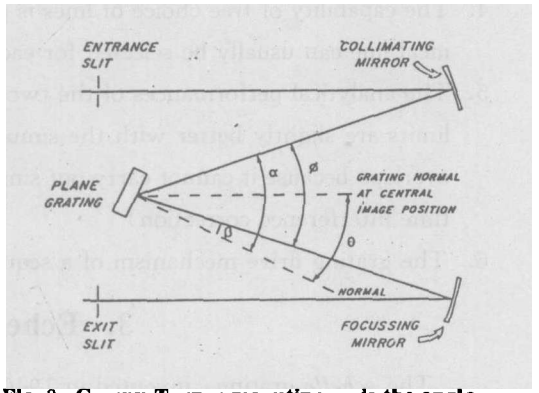

Fig 3 Czerny-Turner mounting. α is the angle of incidence. β is the angle of diffraction, θ is the grating angle measured relative to the zero order normal. and φ is the fixed angle between the incident and diffracted rays.

A new gear reduction mechanism--the harmonic drive have been introduced recently for wavelength scanning [4]. It is a 200 to 1 single-stage reduction system, has a very long operating life and exceptional positional repeatability, and is very fast, scanning across the complete spectrum in less than 2 sec. As shown in Fig. 4, it consists of only three parts: The *elliptical drive shaft* from the stepper motor deforms the *flexible spline* (attached to the grating) to a similar elliptical shape to engage teeth with the circular *rigid spline* (fixed to the spectrometer) at the major axis of the ellipse while teeth at the minor axis are disengaged. Rotation of the drive shaft causes the engaged portion to rotate at the same rate. Because of a two-teeth difference between the two splines, the flexible spline rotates in the direction opposite the that of the of the drive shaft at a 200 to 1 reduction. Because of the high degree of tooth engagement, it is virtually backlash free.

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2. 4. Simultaneous *vs.* Sequential

Both types of instruments can give satisfactory results in general. However, several factors should be considered for the choice between a simultaneous and a sequential system.

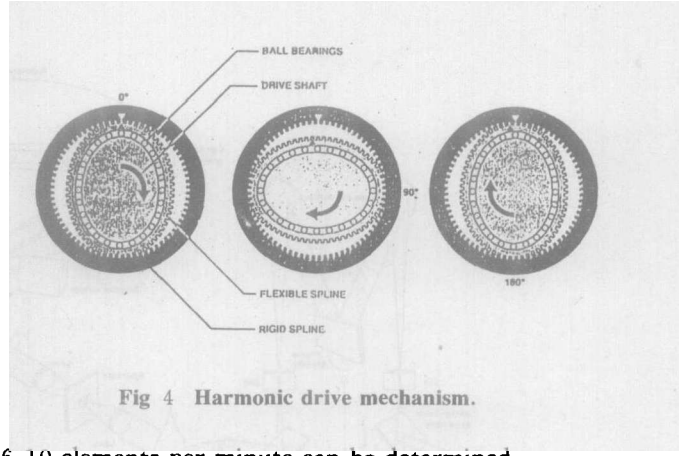

Fig 4 Harmonic drive mechanism.

1. All elements of interest in any sample may be determined in less than 1 minute on a simultaneous instrument; where as on modern rapid-scanning sequentials, 6-10 elements per minute can be determined.
2. The price of a sequential is about 60-70% of that of a simultaneous, but the cost per analysis is higher when using the sequential.
3. The simultaneous is ideal for most high-volume, high-throughput analytical laboratories where elements of interest can usually be predicted and factored into the instrument's custom manufacture. For less predictable workloads (*e. g.* research laboratories), the sequential is more flexible and capable of determining any element that can be of interest.
4. The capability of free choice of lines is perhaps the main strength of the sequential, in that an ideal line can usually be selected for each application.
5. The analytical performances of the two systems at the same line are similar, but the detection limits are slightly better with the simultaneous. The sequential can not deal so well with line overlaps because it cannot carry out simultaneous measurement of the interfering element (real time interference correction)
6. The grating drive mechanism of a sequential is subject to wear.

3. Echelle Spectrometers

The *echelle* grating, invented in 1940 and developed by Prof. G. R. Harrison of MIT [5], provides high resolution by using spectra of very high orders, while maintaining wide spectral ranges with high blaze efficiency. Spectrometers using echelle grating in combination with a prism or a low-resolution grating for cross dispersion (order separation), though compact in size, provide a two dimensional spectral pattern covering the entire useful wavelength range, with resolution of better than 0.01 nm bandpass in the UV. The echelle spectrometer can use PMTs or solid-state two dimensional array detectors, such as CCD, CID or SCD. This type of spectrometer has been gaining popularity in recent years.

Fig. 5 shows schematically an echelle spectrometer, together with its two-dimensional spectral pattern, while Fig. 6 shows a newly developed double pass spectrometer which is claimed to have reduced astigmatism and better image fidelity [6]. This spectrometer employs end-on viewing of the ICP source to match the entrance aperture of the spectrometer (Fig. 7).

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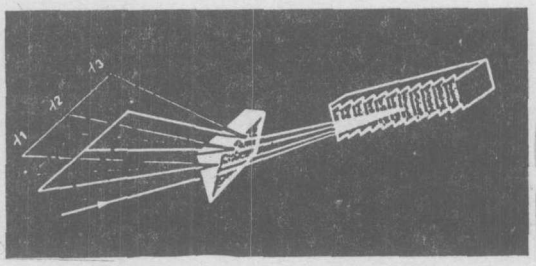

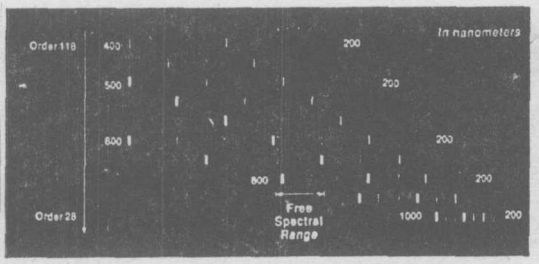

Fig 5 Echelle grating in combination with quartz prism provides unique two dimensional spectral pattern.

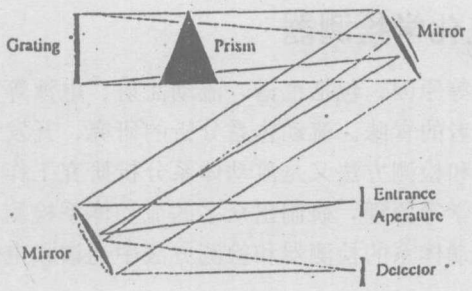

Fig 6 New patented double pass echelle spectrometer reduces astigmatism and provides better image fidelity over a wide range of view.

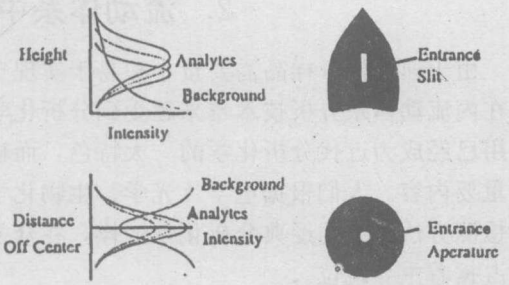

Fig 7 End-on viewing provides an optical axis along which all analyte emission is optimal.

References

[1] R. M. Barnes, R. F. Jarrell, *Gratings and Grating Instruments*, in EL Grove, ed., *Analytical Emission Spectroscopy*, Chap. 4, Part I, Dekker, New York, 1971.

[2] J. W. Olesik, *Spectrometers*, in *Inductively Coupled Plasma in Emission Spectroscopy*, Ed. PWJM Boumans, Part I, Chap. 8, Wiley-Interscience, New York, 1987.

[3] M. Thompson and J. N. Walsh, *A Handbook of Inductively Coupled Plasma Spectrometry*, Chap. 3. Blackie, Glasgow, 1983.

[4] D. Nygaard," *A new concept in wavelength scanning mechanism for sequential spectrometer*," *Proc. Iv Beijing Conference and Exhibition on Instrumental Analysis*, 1991, *Part C. Spectroscopy*, P. C51.

[5] G. R. Harrison, *J. Opt. Soc. Am.*, 39, 522 (1949).

[6] D. Nygaard. Private communication, 1993.

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