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WAVELENGTH DISPERSING DEVICES FOR

SOFT AND ULTRASOFT X-RAY SPECTROMETERS *

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INTRODUCTION

Spectrographic analysis of light elements by soft and ultrasoft fluorescent x-rays has become a useful technique for many applications of elemental analysis, using single crystals, soap multilayers and a combination of total reflection and filtering.

Instead of the wavelength dispersive method based on Bragg reflection which provides high resolution combined with low reflecting intensity, monochromatization combining total reflection by a selected mirror and an appropriate filter offered an alternative approach in order to increase measurable intensity with reasonable spectral resolution.

Recently, the use of synthetic multilayers, which are prepared by sputter/evaporation techniques, has been introduced for the detection of soft and ultrasoft x-rays. Studies on the use of these new wavelength dispersing devices have been conducted and it has been found that the reflectivity of these devices is very high compared with single crystals and soap multilayers and that their resolving power is fairly good.

It is the purpose of this report to make comparisons regarding efficiency of reflection, resolving power and x-ray analytical problems for practical applications among long spacing single crystals, soap multilayers, total reflection combined with a selected mirror and filtering and synthetic multilayers. The x-ray analytical capabilities are shown based upon a standard x-ray fluorescence spectrometer equipped with a sealed-off x-ray tube and a gas flow proportional counter with thin film detector window.

EXPERIMENTAL

The x-ray fluorescence apparatus used in this study was a regular sequential x-ray spectrometer, the S/MAX, made by Rigaku Industrial Corporation. An end window type x-ray tube with a Rh-target and thin beryllium window, namely a Machlette OEG-75, was employed as the excitation source. The fluorescent x-ray of various light elements were monochromatized in vacuum by combining primary and secondary soller slits and flat

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dispersing devices. The dimension of the primary soller slit was 10cm length and 0.45mm spacing (full angle: 0.52 degrees).

The monochromatized fluorescent x-rays were detected by a gas flow proportional counter with thin mylar film window, covered with a thin aluminum metal layer, coupled with a low noise preamplifier. Because of the broadness of the pulse height distribution in soft x-rays, namely approximately 100% energy resolution, optimization for operating conditions of a pulse height selector influences the ratio of signal to background intensity.

It is well known that an analyzing crystal emits fluorescent x-rays of component elements resulting from excitation by incident x-rays.

Because the substrate of the synthetic multilayers is a single crystal wafer of silicon, fluorescent x-rays of Si-K α and of the measured element can be detected by a proportional counter at the Bragg angle for the measured element x-rays.

Figure (1) shows the pulse height distribution curve for fluorine measurement with a synthetic multilayer as well as that for TLAP in which Ti-M series x-rays are exhibited. When the energy difference between Si-K α and measured element x-rays becomes small, monochromatization using pulse height selection is not effective and an increase in background intensity may be found.

Table (1) is the list of dispersing devices used. In this study, TLAP, lead stearate soap multilayer, synthetic multilayers and total reflection mirror with a filter were employed. The mirror used for total reflection of various long wavelength x-rays was a flat glass plate having a smooth surface, combined with a specific filter.

EXPERIMENTAL RESULTS AND DISCUSSIONS

1) Comparison of Reflected Peak Intensity Related to TLAP Crystal

In the comparison of reflectivity of dispersing devices, a narrow x-ray beam (5 x 5mm) was used in order to minimize the influences of optical geometry. Since the TLAP crystal is very popular, measured peak intensity is expressed in values relative to the intensity of TLAP, as shown in Figure (2). It is clear that the intensity of a lead stearate multilayer is 0.2 - 0.3 and the intensities of synthetic multilayers are very high. As the spacing of synthetic multilayers becomes longer,

Figure 1 — Pulse Height Distribution Curve of F-K α Measurement

Table 1 — Used Dispersing Devices for Soft and Ultrashort X-Rays

Measuring x-ray range	55 ~ 98 (713 ~ 676 Å)	
Dispersing devices	TLAP	25.763 Å
	Lead Stearate Multilayer	100.7 Å
	Synthetic Multilayer	I 41.1 Å
		II 69.7
		III 50.6
		IV 58.0
	Total Reflection Mirror	
Applications	B.C.N., No. 109

Figure 2 — Relative Peak Intensity of Various Dispersing Devices

Figure 3 — Relative Peak Intensity of Various Dispersing Devices

an increase of the reflected peak intensity is found. Since the spacing material of SM-II is carbon, a decrease of reflected intensity is found for O-K x-rays.

2) Comparison of Reflected Peak Intensity Related to SM-III

For long wavelength x-rays, a lead-stearate soap multilayer, synthetic multilayers and total reflection mirrors were investigated; the experimental results are shown in Figure (3). The measurement was made by means of a narrow beam similar to the measurement with a TIAP crystal.

Total reflection measurements were carried with a flat glass plate having a smooth surface combined with a specific filter. For comparison, the measured peak intensity is expressed in values relative to the intensity SM-III.

In the case of C-K α x-ray measurement a decrease of relative intensity is found, because the spacing material of SM-II is silicon, which has high absorption for C-K α x-rays.

SM-IV or total reflection with a filter should be adopted for B-K α and C-K α measurement, because the reflectivity of a lead-stearate multilayer is approximately 0.1 from O-K α to C-K α ; for O-K α , that of TIAP is 0.12.

3) Width of Peak Profile

The width of a peak profile is dependent on the perfection of a single crystal or a layer structure, scattering angle and open angle of a soller slit. When a single crystal or layer structure has a perfect periodical arrangement, sharp diffracted x-rays can be detected because of good coherent conditions. A peak profile and its width are strongly dependent on the open angle of a soller slit and are little influenced by scattering angle.

If dispersing devices have a poor periodical arrangement, line broadening is found at larger scattering angles because of the watted effect of the Bragg reflection condition and the degree of perfection of the single crystal or stacking layers.

In Figure (4) the measured width at 50% and 100% of peak intensity maximum is shown.

Figure 4 — 50% and 10% Peak Intensity Width

At small 2θ angles the measured width is defined as the open angle of the soller slit; therefore, it is said that synthetic multilayers have fairly good structure and the reflectivity and the resolution of measured x-rays can be controlled by the open angle of the soller slit.

At large angles, they are largely influenced by the imperfection of stacking layers and the angular dispersion derived from the Bragg equation.

In the case of O-K α x-rays, using a TiAP crystal, the half-width at peak maximum and width at 10% intensity are 2.1 degrees and 6 degrees, respectively, and for F-K α x-rays, the half-width is 1.2 degrees and the 10% width is 2.5 degrees.

4) Relationship Between Dispersion and Width of Peak Profile

In the relationships between 2θ angle of measured x-rays and 50% and 10% width of the peak profile, increases of 50% and 10% widths can be found with increasing 2d spacings of the synthetic multilayers.

Combining the increase of width and the decrease of angular dispersion which arises from large 2d spacing, poor angular resolution should be expected.

In Figure (5) comparisons between measured peak profiles of SM-III and SM-IV are shown, in which the angular distance of 2θ of SM-IV is about 0.4 of that of SM-III.

APPLICATION

1) Boron Detection in Glass

When boron oxide is analyzed in a glass sample, 3rd order x-rays of O-K α (23.6) and B-K α (67.6) are found at the same angle.

Figure 5 — Peak Profile and Dispersion of Synthetic Multilayers

In Figure (6) peak profiles of 3rd order x-rays of O-K α and of B-K α x-rays are shown, where the peak profile was measured using the pulse height selection condition for O-K α and B-K α respectively.

Since the energy resolution of a gas flow proportional counter is approximately 100% for B-K α x-rays, the influence of O-K α overlapping cannot be eliminated completely. The ratio of signal to background intensity is worse and it is very similar to the results obtained by total reflection techniques.

Figure (7) shows the relationship of measured B-K α intensity to B₂O₃ content, as determined chemically in glass samples, using SM-IV.

The simple statistical error for a 10 wt% sample of B₂O₃ was 0.4 wt%. Using the least square method, the analytical accuracy was 0.91 wt% for contents between 2.5 wt% and 19 wt%.

2) Carbon Determination in Steel

In Figure (8) the strip chart recordings of pure samples of component elements normally found in steel samples are shown, using SM-IV, which has high reflectivity but poor resolution because of its large spacing. The skirt of M series x-rays of molybdenum and niobium and N-series x-rays of tantalum and tungsten overlap the C-K α x-rays. In order to check electronic noise and background intensity, x-rays emitted from aluminum metal were shown near the bottom line of the figure for comparison.

In Figure (9) the measured results of the strip chart recording for SM-III are shown. Although the intensity ratio of SM-III to SM-IV is about one tenth or less, because of the small spacing, the dispersing

Figure 6 — Boron Detection in Glass

Figure 7 — Relationship Between Measured B-K α Intensity in B₂O₃ Content in Glass

Figure 8 — Long Wavelength X-Ray Spectra in the vicinity of C-K α X-Rays using SM-IV (158.0 Å)

Figure 9 — Long Wavelength X-Ray Spectra in the vicinity of C-K α X-Rays using SM-III (180.6 Å)

spectra are obtained and the reduction of overlapping influences can be expected when comparing with the results from SM-IV.

The factors of overlapping influences on C-K α x-ray measurement can be expected to be the same as for total reflection techniques.

For the purpose of looking into the details of practical steel samples, the measured results of strip chart recording are shown in Figure (10).

In the upper part of the figure, the results of specially prepared samples, containing about 20 wt% of tungsten and about 7 wt% of molybdenum, are shown.

In the lower part of the figure, the results of carbon steel containing 0.46 wt% of carbon and the position of C-K α x-rays are shown.

The overlapping influences of second order x-rays of Fe-K α , 1 β , and L γ can be found even though pulse height discrimination is applied. When the total reflection technique with a specified filter is applied, there is no influence of Fe-L series x-rays.

In Figure (11), the relationship of measured intensity of C-K α x-rays versus carbon content, as determined chemically, using the SM-IV device, is shown. As mentioned in the previous section, the overlapping influences of molybdenum, niobium and tungsten are clearly shown. For the tool steel samples with higher content of molybdenum and tungsten, an increase in their x-ray intensity is found. An intensity reduction for background x-rays is found compared with that of the total reflection technique.

In Figure (12) are shown the mathematical equations for the determination of carbon content in carbon, low alloy and tool steels. In order to improve the analytical accuracy, overlapping and absorption

Figure 10 — C-K α Detection in Steel in the Case of SM-IV (150.0 Å)

Figure 11 — Relationship Between C-K α Intensity and Carbon Content in Steel

Figure 12 — Carbon Determination in Carbon, Low Alloy and Tool Steel

corrections were applied. For the determination of correction factors for molybdenum, niobium and tungsten binary alloy samples having low carbon content were used. The absorption correction factor of silicon was determined by the use of least square methods using carbon and low alloy steel.

As the standard deviation of a simple statistical error was 0.15 wt% at a content of 1 wt% carbon, the analytical accuracies are two or three times larger than the values of the simple statistical error.

3) Nitrogen Detection

The left side of Figure (13) shows the relationship of nitrogen content and simple calculated intensity of various chemicals versus measured intensities, which are very low because of the high absorption of the detector window material.

Measured intensities versus nitrogen content show scatter because of the absorption effect of matrix elements and the overlapping influences of equal or nearly equal wavelength x-rays and of higher order x-rays.

The right side of Figure (13) shows the relationships between measured and calculated intensity using a simple intensity-weight percent formula (nitrogen content (wt%) is divided by sample mass absorption coefficient for N-K α x-rays). High intensities for TiN and Ba(N₃)₂ are observed because of the overlapping influence of Ti-L α and 2nd order x-rays of Ba-M α and MB.

Compared with the total reflection technique for the analysis of nitrogen, the synthetic multilayer is superior, because the total reflection method has poor resolution.

Figure 14 — Fluorine Determination in Cement

Figure 13 — Measured Intensity of N-K α X-Rays Versus Nitrogen Content and Simple Calculated Intensity of Various Chemicals

4) Fluorine Determination in Cement

In Figure (14), the relationship between measured x-ray intensities of F-K α x-rays and fluorine content is shown for various dispersing devices. For SM-IV, high background intensity and scattered intensity of measured samples are found. Because of the small dispersion, higher order x-rays of Si-K α and Al-K α interfere with F-K α x-rays.

In the case of SM-II and SM-III, overlapping influences of Fe-L α and a small increase of background intensity are found in the specified samples. Since the experimental results obtained by SM-I and T1AP exhibit good calibration curves with reasonable analytical accuracies, SM-I or T1AP crystal is recommended for the analysis for fluorine.

CONCLUSION

Synthetic multilayers have been studied as dispersing devices with emphasis on their essential characteristics which are reflecting efficiency, resolving power and x-ray analytical problems for practical applications. They were found to be very effective for x-ray fluorescence analysis in the soft and ultra soft x-ray region.

The synthetic multilayer has high reflectivity, but its resolving power is not high compared with a T1AP crystal and soap multilayers. For short wavelength x-rays synthetic multilayers having a small spacing have to be used, in order to obtain dispersion and low background intensity. For long wavelength x-rays, synthetic multilayers having long spacings, with carbon spacing material, should be used to obtain higher reflectivity.

For general applications, it is necessary to study background intensity and overlapping conditions before x-ray measurement, since these devices have relatively poor resolving power and high possibility of overlapping influences.

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