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X-RAY FLUORESCENCE SPECTROMETERS

A COMPARISON OF WAVELENGTH AND ENERGY DISPERSIVE INSTRUMENTS

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ABSTRACT

Wavelength dispersive and energy dispersive x-ray fluorescence spectrometers are compared. Separate sections are devoted to principles of operation, sample excitation, spectral resolution, and x-ray detection. Tabulated data from the literature are cited in the comparison of accuracy, precision, and detection limits. Spectral interferences and distortions are discussed. Advantages and limitations are listed for simultaneous wavelength dispersive spectrometers, sequential wavelength dispersive spectrometers, and Si(Li) energy dispersive spectrometers. Accuracy, precision, and detection limits are generally superior for wavelength dispersive spectrometers.

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X-RAY FLUORESCENCE SPECTROMETERS –

A COMPARISON OF WAVELENGTH AND ENERGY DISPERSIVE INSTRUMENTS

INTRODUCTION

Two types of x-ray fluorescence spectrometers are commercially available: wavelength dispersive and energy dispersive. Both types analyze fluorescent x-rays and produce x-ray spectra for qualitative and quantitative analyses. The different methods used to resolve the sample x-ray beam into its spectrum distinguishes one type from the other and imparts certain advantages and limitations to each depending upon the specific analysis.

The principal advantages of wavelength dispersion over energy dispersion are superior resolution for low energy (<15 keV) x-rays, high count rate capability, and analysis of only x-rays of interest. Advantages of energy dispersion are design simplicity with no moving parts, simultaneous detection and display of all elements, and high geometric and detection efficiency making low-power excitation practical.

The sequential wavelength dispersive spectrometer is extensively used because it is highly accurate and very versatile. It is well suited to research applications with low or moderate sample loads. A total elemental analysis may require as much as 30 minutes per sample.

The simultaneous wavelength dispersive spectrometer is normally used for routine production quality control requiring rapid and highly accurate analysis of specified elements on large numbers of samples. A total elemental analysis including computer printout of results typically requires less than one minute.

Energy dispersive spectrometers are widely used for research and production quality control. They are also used extensively with scanning electron microscopes and electron probe analyzers because the Si(Li) detector is compact and sufficiently sensitive to operate at the low beam currents typical of these instruments. Energy dispersive spectrometers determine the major elements in a sample in two minutes or less, but are generally less accurate and less precise than wavelength dispersive spectrometers.

PRINCIPLES OF OPERATION

The basic components of a wavelength dispersive x-ray spectrometer are shown in Figure 1.[1] These components consist of an x-ray tube to irradiate the sample and to induce atomic fluorescence, a crystal monochromator to disperse the polychromatic sample x-rays, and a detector to quantitatively determine the intensity of the monochromatic spectral components.

The design of each monochromator is based on the Bragg Law: $n\lambda = 2d \sin \theta$. This law relates the wavelength λ of the detected x-ray beam to the interplanar spacing of the analyzing crystal diffraction planes d. n is an integer numerically equal to the x-ray difference in wavelengths for successive planes, and θ is the Bragg angle, the angle between the incident x-rays and the diffracting planes.

The intensity at one selected wavelength is determined by choosing an analyzing crystal with an appropriate d value and by accumulating data with the crystal and detector accurately positioned at θ and 2θ, respectively, from the incident x-ray beam. In simultaneous spectrometers, a separate monochromator-detector system is used to determine the x-ray intensity at each wavelength of interest. All monochromators operate simultaneously during an analysis; hence the name simultaneous wavelength dispersive x-ray spectrometer. A spectrometer with only fixed monochromators does not produce an x-ray spectrum; it gives only the intensities at selected wavelengths for the elements of interest.

Scanning capability is normally provided in simultaneous wavelength dispersive spectrometers by replacing one or more fixed monochromators with scanning monochromator. Wavelength dispersive x-ray spectrometers designed to operate primarily in the scanning mode are called sequential x-ray spectrometers. A scanning monochromator is designed with the same basic components as a fixed monochromator but includes a mechanism to slowly change θ and 2θ so that the detector intercepts the diffracted beam over the range of θ values permitted by the crystal. A spectrum of x-ray intensity versus wavelength can thus be produced. A scanning monochromator can also be preset and used as a fixed monochromator for analysis of elements of only occasional interest.

An energy dispersive x-ray spectrometer is illustrated in Figure 2 showing direct and secondary target excitation.[2] Sample fluorescence is normally induced by direct irradiation with x-rays or gamma rays or by irradiation with filtered x-rays from a secondary target. Charged particle excitation is also used in special applications.

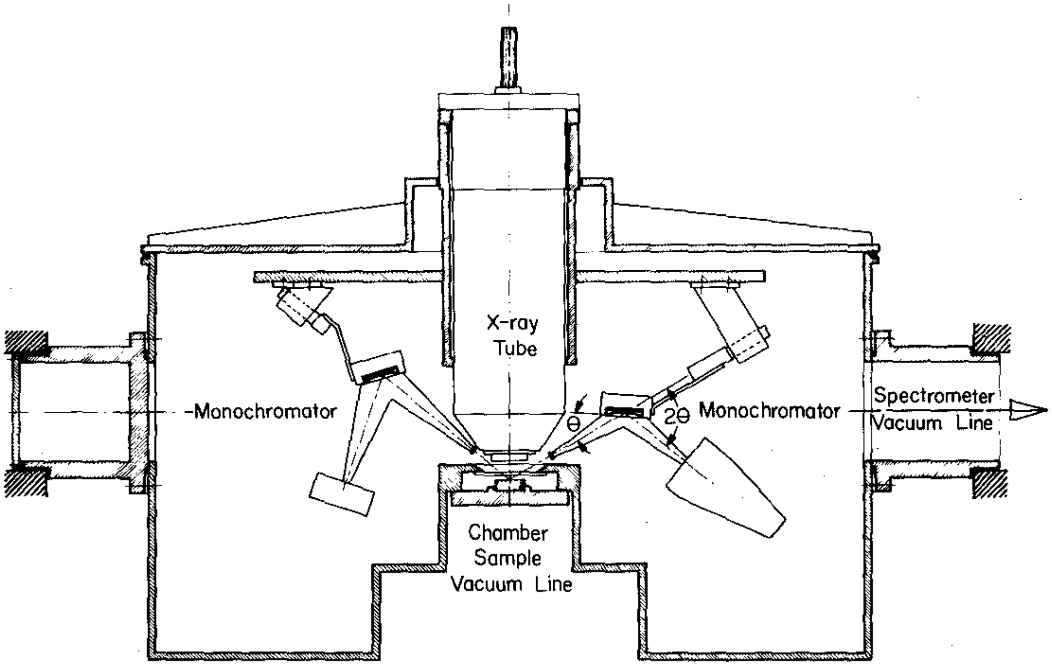

FIGURE 1. Simultaneous Wavelength Dispersive X-Ray Spectrometer Showing Two Monochromators[1]

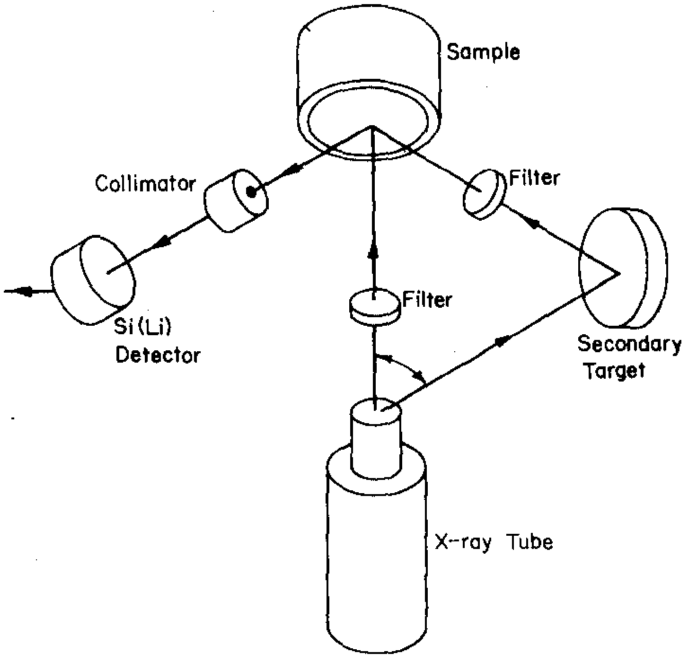

FIGURE 2. Energy Dispersive X-Ray Spectrometer Showing Direct and Secondary Target Excitation[2]

The polychromatic fluorescent x-rays from the sample are collimated and directed to a Si(Li) semiconductor detector. The sample x-ray beam arrives at the detector undispersed; it is resolved electronically into its spectral components by pulse-height analysis of the detector signals. The pulse-height analysis produces a multichannel spectrum of x-ray intensity versus x-ray energy.

The energy range of the spectrum is operator-selected to include the elements of interest by appropriate instrument settings. The x-ray spectrum is accumulated simultaneously over the selected energy range by the single Si(Li) detector. The spectrometer has no moving parts and has no components requiring precise alignment.

EXCITATION

Conventional wavelength dispersive x-ray spectrometers excite sample fluorescence with the continuous x-ray spectrum from high-power (2500-4000 watts) x-ray tubes. High-power x-ray generation is necessary because the overall efficiency of wavelength dispersive spectrometers is low. Only a small fraction of the total sample x-rays is actually analyzed because the solid angle subtended by the crystal monochromator is small. Further intensity losses occur at the analyzing crystal and, depending upon the detector efficiency, at the detector.

An electron gun is available as an accessory for sample excitation on the Applied Research Laboratories X-Ray Quantometer 72000.[1] Electron excitation gives a greater x-ray yield for light elements than conventional x-ray excitation but requires conductive samples and a high vacuum system.

Energy dispersive x-ray spectrometers excite sample fluorescence with x-rays, gamma rays, or charged particles. Gamma ray excitation and charged particle excitation are generally used for special applications where their respective advantages are significant. Gamma ray excitation requires no utilities and offers a light weight, compact, and very stable monochromatic source with very low background. Limitations of gamma ray excitation are the small selection of excitation energies available in radioisotope sources, their low maximum intensity, and the special care and handling they require.

Charged particle excitation, especially with electrons, has been extensively used for special applications such as scanning electron microscopes and electron probe microanalyzers. Charged particle excitation is, however, not generally available on conventional energy dispersive x-ray spectrometers.

X-ray irradiation is the most common method of sample excitation for x-ray spectrometry. X-ray generators are safe, are dependable, and have high power capability. Energy dispersive x-ray spectrometers of the secondary target type require high intensity sources to overcome intensity losses at the secondary target and filter. High power x-ray generators meet this need. The major advantages of secondary target excitation are low background and the broad selection of excitation conditions through appropriate selection of x-ray tube anodes, x-ray filters, and secondary targets.

Energy dispersive x-ray spectrometers that use direct irradiation for sample excitation require less intense sources. Low power (<50 watts) air-cooled x-ray generators or gamma-emitting radioisotope sources provide sufficient excitation for these spectrometers.

Recent development of pulsed x-ray tubes has significantly improved the performance of x-ray excited energy dispersive spectrometers, especially those using low power bremstrahlung excitation. By pulsing the x-ray tube at a frequency related to the recovery time of the detection system, sample x-rays arrive at the detector only when the detector is ready to process them. The advantages of pulsed x-ray excitation over continuous excitation result from the decrease in percent deadtime for a specified count rate. These advantages are most fully realized at high count rates. They include decreased analysis time, decreased peak centroid shifts, and increased signal-to-noise ratio.

RESOLUTION

The ability of a spectrometer to distinguish between or resolve adjacent spectral peaks is known as resolution. The resolution of a wavelength dispersive x-ray spectrometer is determined primarily by the resolving power of the diffraction crystal. The resolution of an energy dispersive x-ray spectrometer is determined by the detector and associated electronics. The relative energy resolution of an x-ray spectrometer may be quantitatively defined in percent for a single peak as 100 times the full width at half maximum (FWHM) expressed in energy units divided by the mean energy of the peak. Small values for the relative resolution indicate good resolution; large values indicate poor resolution. Figure 3 compares the resolution of a flow-gas proportional detector, a Si(Li) energy dispersive detector, and lead stearate decanoate (PbSD), potassium hydrogen phthalate (KAP), ammonium dihydrogen phosphate (ADP), and lithium fluoride (LiF) diffraction crystals typically used in wavelength dispersive x-ray spectrometers.[3]

The resolution of the wavelength dispersive spectrometer is vastly superior to that of the energy dispersive spectrometer at low energies. This superiority is clearly illustrated in Figure 4 by the spectra of Birks and Gilfrich.[4] They determined the resolution of the potassium K_α x-ray line (3.3 keV) to be 3 eV for wavelength dispersion and 150 eV for energy dispersion. Their spectra of normal amounts of cadmium and potassium in air pollution samples show the effect of poor resolution. With energy dispersion, the cadmium L_α line would not be detected because of the strong overlap by potassium. With wavelength dispersion, the cadmium L_α line is completely resolved and easily measured.

The resolution of both energy dispersive and wavelength dispersive spectrometers becomes poorer as x-ray energy increases. Figure 3 shows that wavelength dispersive and energy dispersive spectrometers have similar resolution of 260 eV for 17 keV x-rays. Above 17 keV, energy dispersion gives better resolution than does wavelength dispersion. Typical resolutions at 25.2 keV (tin K_α) are 800 eV for wavelength dispersion and 280 eV for energy dispersion.

The excellent resolution of wavelength dispersive spectrometers over most of the energy region of analytical interest is a major factor contributing to accurate and precise analyses. Wavelength dispersive spectral peaks are narrow with well-defined backgrounds on each side. The background under a spectral peak can be accurately estimated by interpolation as the total counts under a straight line through the adjacent background regions. Typical peak-to-background ratios for wavelength dispersive analyses are from 500 to 1000. In contrast, low energy peaks of energy dispersive spectra are broad and poorly resolved from those of neighboring elements. Backgrounds adjacent to each peak are not well defined and may introduce significant errors in both net peak and peak background estimates when determined by interpolation from adjacent background regions. Mathematical unfolding of peaks of energy dispersive spectra is frequently necessary to compensate for poor resolution. Typical peak-to-background ratios for energy dispersive spectra of pure materials are in the order of only 50.

Some analyses can be satisfactorily performed by wavelength dispersive spectrometers because of their superior resolution but not by energy dispersive spectrometers. The analysis of manganese and cobalt in stainless steel is a classic example. With wavelength dispersion, manganese K_α x-rays can be resolved from chromium K_β x-rays, and cobalt K_α x-rays can be resolved from iron K_β x-rays. The spectrometer must be capable of resolving lines separated by only 52 eV. Energy dispersive spectrometers with resolution of over 200 eV in this energy range cannot satisfactorily determine manganese or cobalt in stainless steel.

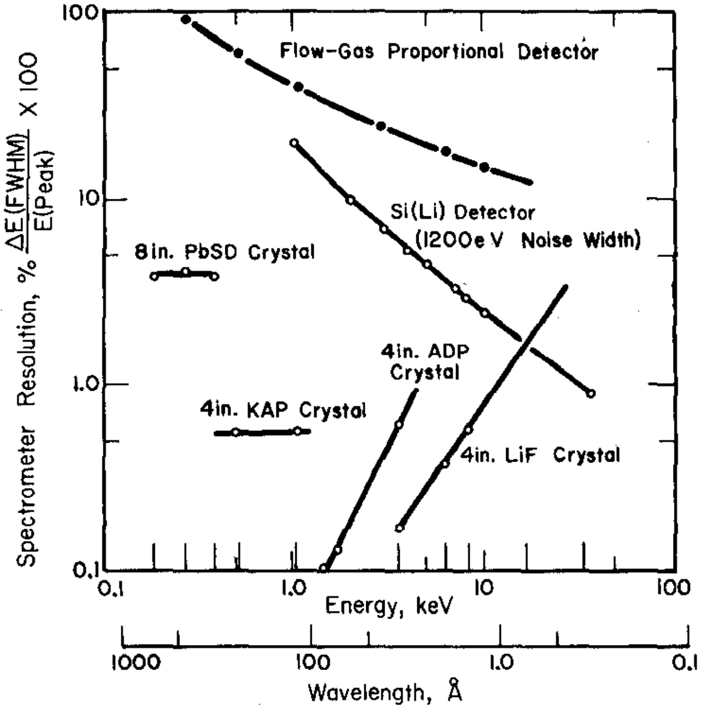

FIGURE 3. Comparison of Resolution Between Wavelength and Energy Spectrometers as a Function of X-Ray Energy[3]

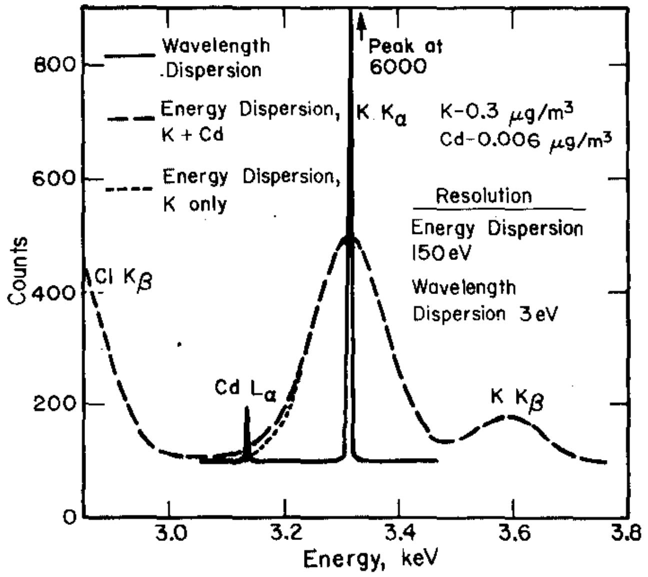

FIGURE 4. Comparative Resolution of Cadmium and Potassium X-Rays by Wavelength Dispersion and Energy Dispersion[4]

Radioactive samples with high gamma levels can be analyzed by wavelength dispersion, but can be analyzed poorly, if at all, by energy dispersion. With wavelength dispersion, the crystal disperses the radiation so that only the x-rays of interest reach the detector. The detector can be shielded from direct gamma irradiation of the sample. With energy dispersion, the detector cannot be shielded. The high level of gamma radiation saturates the detector, drives the deadtime to 100%, and prevents accumulation of data.

DETECTION

Three types of detectors are commonly used on wavelength dispersive x-ray spectrometers: flow gas proportional counters, sealed gas proportional counters, and scintillation counters. Flow counters are used to detect low energy x-rays. Flow counter windows are made of thin polymer films because the films are transparent even to most low energy x-rays. Common flow gases are argon-methane and helium-carbon dioxide.

Scintillation counters or sealed xenon or argon proportional counters are used on wavelength dispersive x-ray spectrometers to detect higher energy x-rays. For the K_α lines of elements with atomic numbers 40 to 51, the scintillation counter, typically thallium-activated sodium iodide, NaI(Tl), has greater counting efficiency than either the argon or xenon sealed proportional counter.

Energy dispersive x-ray spectrometers use Si(Li) detectors almost exclusively. Si(Li) detectors are highly efficient and provide better resolution for pulse-height analysis than either flow gas proportional counters or NaI(Tl) scintillation counters.

Typical detector efficiencies are shown in Figure 5 for several x-ray detectors.[5] The NaI(Tl) scintillation detector and the Si(Li) semiconductor detector are highly efficient over a broad energy range. Flow gas proportional counters have high efficiency at low x-ray energy, but are rather inefficient at higher energies. Sealed proportional detectors are generally less efficient than NaI(Tl) detectors.

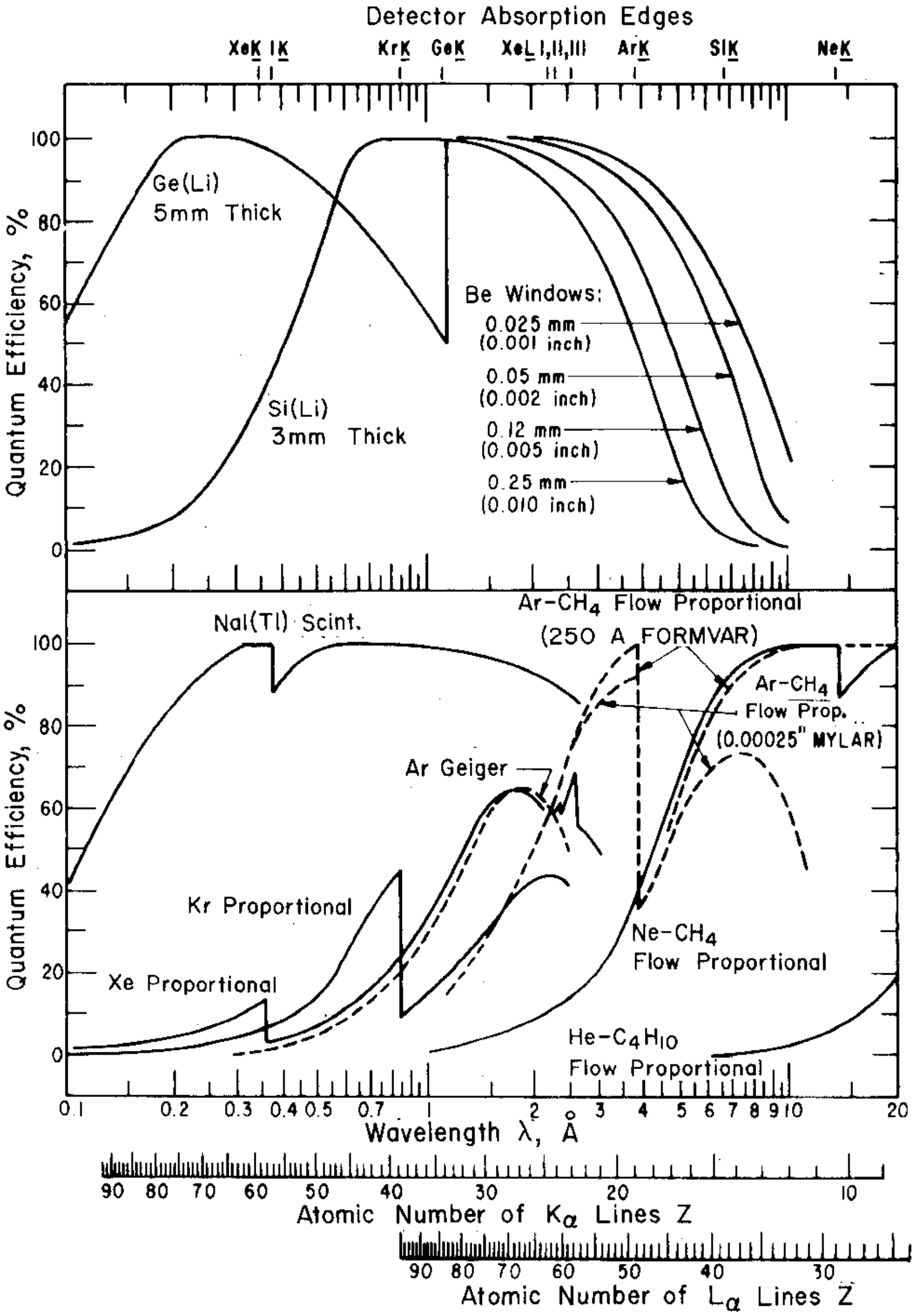

FIGURE 5. Typical Quantum Efficiencies of Several X-Ray Detectors[5]

ACCURACY, PRECISION, AND DETECTION LIMITS

The accuracy and precision of wavelength dispersion analyses are generally superior to those of energy dispersive analyses. This superiority was clearly demonstrated by Beaman and Solosky[6] who analyzed several well-characterized alloys for 55 elements by energy dispersion and wavelength dispersion on an electron probe analyzer with one energy dispersive and four wavelength dispersive spectrometers. They concluded that for concentrations greater than 23 wt % relative errors of 6% can be expected with energy dispersive analysis when energy interferences are absent. About one-fourth of these errors will be less than 1%. In the 5 to 20 wt % range, relative errors will be about 10% with one-fifth of the errors less than 1%. Large relative errors may be encountered at low concentrations. Their analysis of these alloys for the 55 elements by wavelength dispersion were more accurate and more precise. The standard deviation of all relative errors was only 2% by wavelength dispersion, and over three-fourths of these errors were less than 1%.

Single element detection limits[7] for wavelength dispersive spectrometers are compared in Table 1 for analysis of 13 elements on air pollution filters. Extrapolated values indicate the detection limits that could be obtained with improved state-of-the-art equipment. These data show that the detection limit is generally lower for wavelength dispersive analysis than for energy dispersive analysis. Gilfrich, Burkhalter, and Birks[7] emphasize that the detection limits of Table 1 are those for single elements determined on standards containing no interferences and caution that the tabulated limits for energy dispersive analysis may not be attainable on real samples. They conclude that major and intermediate concentrations can be analyzed by either wavelength or energy dispersive spectrometer using x-ray tube excitation. Elements present at the lowest detectable concentrations can be measured only by wavelength dispersion because of the limitations imposed by poor resolution and low count rate of energy dispersion.

TABLE 1

100-Second Detection Limits[7] for Various X-Ray Techniques, ng/cm^2

Wavelength Dispersion	*Al*	*S*	*K*	*Ca*	*V*	*Fe*	*Cu*	*Zn*	*Se*	*Br*	*Zr*	*Pb*
X-ray tube excitation as measured (900 watts)												
Cr Tube	360	52	3	10	53	150	160	180	820	390		1000
Rh tube	85	13	18	29	33	30	49	51	150	210		260
W tube		52			29	36	40		100	160		
Extrapolated to 2500 watts												
Cr tube	220	31	2	6	32	90	96	110	490	230		600
Rh tube	50	8	11	17	20	18	29	31	90	130		160
W tube		31			17	22	24		60	100		
Energy Dispersion												
Isotope excitation as measured												
7 MCi ^{55}Fe[a]				110	180							
69 mCi ^{109}Cd				6200	2100	2200		1400	420		230	700
Extrapolated to 150 mCi												
^{55}Fe				84	130							
^{109}Cd				3200	1100	1200		740	220		120	370
Fluorescer excitation as measured (900 watts)												
Mn				58	51							
Cu				62	68	44						
Ag				310	360			180	69		50	190
Cr-Zr				84		350		210	44			
Extrapolated to 2500 watts												
Mn				27	24							
Cu				28	31	20						
Ag				150	170			84	31		23	84
Cr-Zr				38		160		100	20			
X-ray tube excitation as measured (150 watts[b])												
Mo tube				350	160	120		100	48			110
W tube				33	34	39		160	110			190
W tube - Ni foil		570	220	140	90	120		110	81			110
Extrapolated to 10,000 counts/sec[c]												
Mo tube				160	71	53		44	21			49
W tube				19	20	22		92	63			110
W tube - Ni foil		220	84	53	34	46		42	31			42

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[a] Measurement with ^{55}Fe made for 2000 sec because of low activity.

[b] 0.002 steradian aperture between x-ray tube and sample.

[c] 150-watt tube power with aperture produced count rates of: Mo, 5000 counts/sec; W, 10,000 counts/sec, W with filter, 3500 counts/sec. At these count rates, detector resolution varied from 400 to 500 eV.

SPECTRAL INTERFERENCES AND DISTORTIONS

Spectral interferences and distortions that occur with both wavelength and energy dispersive systems can frequently be minimized by careful selection of analysis conditions. Scatter peaks and escape peaks interfere with both energy and wavelength dispersive spectra. Scatter peaks are formed in the pulse-height spectrum by elastic and inelastic interaction of x-rays with sample electrons, especially high energy x-rays with electrons of low atomic number elements.

Escape peaks occur in pulse-height spectra when energy transfer in the detector is incomplete. The intensity of the escape peak relative to the main peak increases for gas detectors with increasing fluorescent yield of the detector gas. The escape peaks for krypton and xenon detectors are more intense than their main peaks. Escape peaks for argon proportional detectors, for NaI(Tl) scintillation detectors, and for Si(Li) solid state detectors are either not excited, relatively small, or not resolved from the main peaks. Escape peaks generally are not a serious problem in x-ray spectrometry.

Spectral distortions may occur during pulse-height analysis. At high count rates, successive photons may arrive at the detector before the detector has fully recovered from detection of the preceding photon. If the second photon arrives during the detector dead period, the pulse will not be counted. This causes nonlinearity at high count rates in a plot of measured intensity versus true intensity and presents a limitation that is especially serious for Si(Li) detectors. If the second pulse arrives after the dead period but before the detector has fully recovered, the pulse will be counted but the pulse height will be abnormally low. This causes a shift in the spectral peak centroid to lower energies and a decrease in resolution (peak broadening). Centroid shift and peak broadening are especially troublesome in pulse-height selection analysis because the peak shape changes and the centroid shifts, but the analysis window remains fixed. Serious intensity effects occur with proportional counters above 5×10^4 counts/second and with Si(Li) detectors above 10^4 counts/second, but they may not be serious with a scintillation counter even at 10^5 counts/second.

Intensity nonlinearity and spectral distortion at high count rates can be minimized by electronic circuitry, which rejects pulses that occur during the detector recovery period. Recent application of pulsed x-ray tubes to x-ray spectrometers has also significantly reduced spectral distortion and analysis time, especially for energy dispersive spectrometers with Si(Li) detectors.

ADVANTAGES AND LIMITATIONS

General advantages and limitations of energy dispersive and wavelength dispersive x-ray spectrometers are presented below. Simultaneous and sequential wavelength dispersive spectrometers are listed separately, because even though they are identical in principle they are significantly different in laboratory applications.

Simultaneous Wavelength Dispersive Spectrometer

Advantages

- Spectral resolution for low energy x-rays is excellent. Resolution of less than 10 eV FWHM is typical below 5 keV.
- High count rate capability is provided by proportional counters (10^5 counts/second) and scintillation counters (10^6 counts/second).
- Spectrometer analyzes only the x-rays of interest.
- Detectors can be shielded from direct radiation of radioactive samples.
- Instrument is extremely rugged because of fixed spectrometers and absence of moving parts.
- Fixed monochromators can be of the full-focusing, curved-crystal type.
- The components (collimators, detector, and crystals) of each channel can be optimized for its specific element.
- Simultaneous measurement of all analytes, internal standards, and backgrounds permits greater economy of analysis time and cost: analysis time is determined by the least intense element.
- Greater sensitivity and precision can be obtained in a given time by setting two or more channels to the same analyte line and combining their outputs.

Limitations

- Instrument is very bulky because of multiplicity of spectrometers.

- High power excitation is required.
- Large numbers of expensive components (collimators, detectors, and crystals) are required.
- Electronic readout is elaborate and complex.
- Homogeneity and surface topography are critical because each spectrometer views sample from a different angle.
- Instrument is rather inflexible because changing preset channel to another analyte line is inconvenient. Simultaneous spectrometers are best suited to routine analysis of large numbers of similar samples.

Sequential Spectrometer

Advantages

- Spectral resolution for low energy x-rays is excellent. Resolution of less than 10 eV FWHM is typical below 5 keV.
- High count rate capability is provided by proportional counters (10^5 counts/second) and scintillation counters (10^6 counts/second).
- Spectrometer analyzes only the x-rays of interest.
- Detectors can be shielded from direct radiation of radioactive samples.
- Instrument is much more compact than simultaneous spectrometer.
- An economical number of collimators, detectors, and crystals are required.
- X-ray tube target, primary beam filter, kV, and mA can be programmed.
- Homogeneity and surface topography are less critical than with simultaneous spectrometer because measured x-rays for all analytes leave the specimen in the same direction.
- Spectrometers are readily indexed to any specified 2θ angle for measurement of any analyte line of background.

Limitations

- Indexing mechanisms are complex.
- Use of curved crystals is not convenient.
- Simultaneous measurement of analytes, internal standards, and backgrounds cannot be realized.
- Analysis time is long and is equal to the sum of the analysis times for each analyte.

Energy Dispersive Si(Li) Spectrometer

Advantages

- Instrument design is simple and involves no moving parts.
- Geometric and detection efficiencies are high.
- Precision drive mechanism, collimators, and crystals are eliminated.
- Intensity loss from inefficient diffraction process is eliminated.
- Recorded spectrum does not contain higher order diffraction lines.
- Low power x-ray tubes or radioisotope excitation sources are practical.
- Entire spectrum is accumulated and displayed simultaneously. This displayed spectrum permits observation and measurement of elements other than those specified for analysis and reduces the probability of overlooking unsuspected elements.

Limitations

- Resolution for x-rays below 15 keV is inferior to that for a crystal spectrometer.
- X-rays below 1 keV are undetected.
- Coincidence losses, pulse-height shifts, and detector choking occur readily.

- Detection limits for those analytes in the presence of strong lines are higher than for crystal spectrometers.

- Detector must be perpetually maintained at liquid nitrogen temperature.

- Detector cannot be shielded from gamma radiation of radioactive samples. Direct gamma radiation of the detector may increase count rate above acceptable levels and may make analysis of highly radioactive samples difficult or impossible.

CONCLUSIONS

The accuracy, precision, and detection limits for wavelength dispersive analyses are generally superior to those for energy dispersive analyses. The excellent spectral resolution over most of the x-ray region of analytical interest and the high count rate capability of wavelength dispersive spectrometers are major factors contributing to the superior performance. The data of Beaman and Solosky[6] indicate that for wavelength dispersive analysis more than three-fourths of all analyses will be accurate to ±1% relative. In contrast, the energy dispersive analysis in the absence of interferences, relative errors of 6 to 10% can be expected for elemental concentrations greater than 5 wt %, and large error may be encountered at low concentrations. Even for major components (>23%), only one-fourth of the relative errors are likely to be less than 1%.

Some analyses can be performed by wavelength dispersive spectrometers but poorly or not at all by energy dispersive spectrometers. For example, manganese and cobalt can be accurately determined in stainless steel by wavelength dispersion but not by energy dispersion because Si(Li) detector resolution is inadequate to resolve the respective K_α lines from the $K\beta$ lines of their neighboring elements. Another example unrelated to spectrometer resolutions is the analysis of samples emitting very high levels of gamma radiation. These samples can be analyzed by wavelength dispersive spectrometers by shielding the detector from direct exposures to the gamma radiation. Shielding of the Si(Li) detector for energy dispersion analysis is not possible, and the intense gamma radiation may saturate the detector and prevent data accumulation.

The analytical capabilities and limitations of wavelength and energy dispersive spectrometers are significantly different. In general, wavelength dispersion is required for highly accurate and precise analyses especially for low atomic number elements in complex matrices, for elements at very low concentrations, and for radioactive samples emitting high levels of gamma radiation. Energy dispersion may be required for low-power applications such as scanning electron microprobes, electron probe analyzers, and spectrometers with isotope excitation.

REFERENCES

1. *X-Ray Quantometer Model 72000, Description.* p 6, Applied Research Laboratories, Sunland, CA (1969).

2. R. Woldseth. *X-Ray Energy Spectrometry.* p 2.53, Kevex Corporation, Burlingame, CA (1973).

3. R. Fitzgerald and P. Gantzel. "X-Ray Energy Spectrometry in the 0.1 to 10 Å Range" presented at the Seventy-Third Annual ASTM Meeting in Toronto, Ontario and published in *Energy Dispersion X-Ray Analysis: X-Ray and Electron Probe Analysis.* pp 3-35, J. C. Russ, Coordinator, American Society for Testing and Materials, Philadelphia, PA (1970).

4. L. S. Birks and J. V. Gilfrich. "X-Ray Spectrometry." *Anal. Chem. 48,* 273-R (1976).

5. E. P. Bertin. *Principles and Practice of X-Ray Spectrometric Analysis.* 2nd Ed., p 268, Plenum Press, New York, NY (1975).

6. D. R. Beaman and L. F. Solosky. "Accuracy of Quantitative Electron Probe Microanalysis with Energy Dispersive Spectrometers." *Anal. Chem. 44,* 1598 (1972).

7. J. V. Gilfrich, P. G. Burkhalter, and L. S. Birks. "X-Ray Spectrometry for Particulate Air Pollution - A Quantitative Comparison of Techniques." *Anal. Chem. 45,* 2002 (1973).