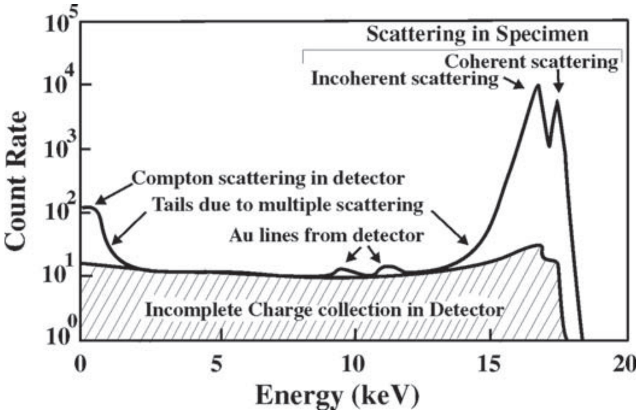

Fig. 1.23. Background contribution in the EDXRF spectrometer with monochromatic excitation at 17.4 keV

analysis. Figure 1.23 illustrates the effect on a pure-water specimen excited by monochromatic excitation i.e., 17.4 keV Molybdenum Kα line from a graphite monochromator on a Molybdenum anode X-ray tube. The excitation X-rays are coherently and incoherently scattered from the water specimen to produce the intense peaks at 17.4 and 16.8 keV, respectively. The incoherent peak is much broader due to the range of scattering angles included about the nominal 90° scattering angle. The low-energy tail on the incoherent peak extending down to about 10 keV is primarily due to multiple Compton scattering in the specimen. The major background is due to incomplete charge collection in the Si(Li) detector which occurs because the holes and electrons produced in the detector by 16.8 and 17.4 keV X-rays combine before these are collected. The result is a pulse of abnormally low-amplitude recorded at a lower than normal energy. Some improvements can be gained by collimating the detector and using only the central 50% of its sensitive area.

Since the gold contact layer in front of the Si(Li) detector are fluoresced by the incoming X-rays, these cause the Au L and Au M X-rays lines in the EDXRF spectrum. The intensity of these lines is a function of the thickness of the gold contact layer and it may vary significantly from detector to detector. The gold L lines are often broadened on the high-energy side due to the ejected photoelectrons recoiling from the gold layer into the detectors' sensitive volume. The silicon escape peaks and the presence of sum peaks also cause hindrance to the analysis of X-rays spectra.

1.9 Methods for Improving Detection Limits

The minimum detectable amount is that concentration of the element that gives a net intensity (I_L) equal to three times the square root of the background intensity $(I_\mathrm{B})^{1/2}$. In the case of X-ray tube exciter, the sensitivity can be greater if constant potential generator is used, kV and mA are as high as possible (but not to decrease $I_\mathrm{L}/I_\mathrm{B}$), target lines lie close to short-side of the absorption edge of its analytical line (usually a target just higher in Z number) and thin X-ray tube window is used.

Since the major background source limiting trace element analysis is the scattered X-ray tube continuum in XRF, a simple and effective means of removing this limitation is the use of a primary beam filter. If a thin aluminum filter is employed, the filtered X-ray tube spectrum of the chromium K-lines will strongly attenuate the chromium lines and all longer wavelengths allow the short-wavelength radiations. Thus a low background region is created for trace elements with longer wavelength. These elements will be excited by the shorter wavelength continuum passing through the filter. It is important to note that the sensitivity (m) for the trace elements will be reduced unless the tube current can be reduced to compensate. However the detection limit will be improved if the ratio $\sqrt{I_\mathrm{B}}/m$ is reduced, which is possible depending on the choice of filter thickness.

In XRF, monochromatic excitation provides good trace sensitivity only over a restricted range of elements close to the selected excitation energy. This occurs because the cross-section for ionizing the appropriate shell in the atom decreases rapidly as the excitation energy is increased above the absorption energy of the analyte element.

Figure 1.24 illustrates the sensitive range for simultaneous trace element analysis as a function of monochromatic excitation energy. The bands are defined, one for the analysis of the Kα line and the other for analysis of the Lα line. The high atomic number boundary on each band is controlled by interferences with the incoherent scattered peak. The starting point is to assume that the highest energy line, which can be analyzed, is of the excitation energy and the absorption edge for this line must also be below the excitation

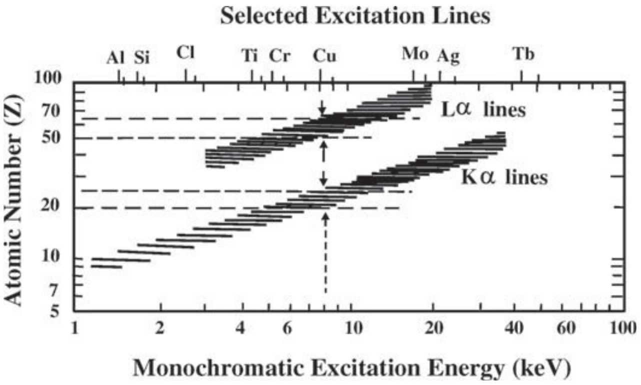

Fig. 1.24. Sensitive range for trace analysis with monochromatic excitation