A new nondestructive accelerator based x-ray fluorescence (AXRF) technique is developed to identify elements in large sample volumes. The technique is based on using high energy pulsed Bremsstrahlung beams (3-6.5 MeV) from small electron accelerators to produce K-shell atomic fluorescence x-rays. This primary photon beam exhibits excellent penetration and high degree of directivity providing samples assaying up to 20 gm/cm$^2$ thick for Z material 30. The fluorescence yield is measured as a function of atomic number, material density and sample size. The high energy primary photons also allow the production of the 511 KeV radiation from positron annihilation inside the sample which is characterized by the electron momentum distribution of the atoms. By detecting these 511 KeV photons with a high energy resolution HPGe detector, we expect to develop a new element identification method. In addition the annihilation count rate is proportional to the average atomic number of the sample. Combining AXRF with annihilation radiation provides a more comprehensive and accurate assay for large samples.