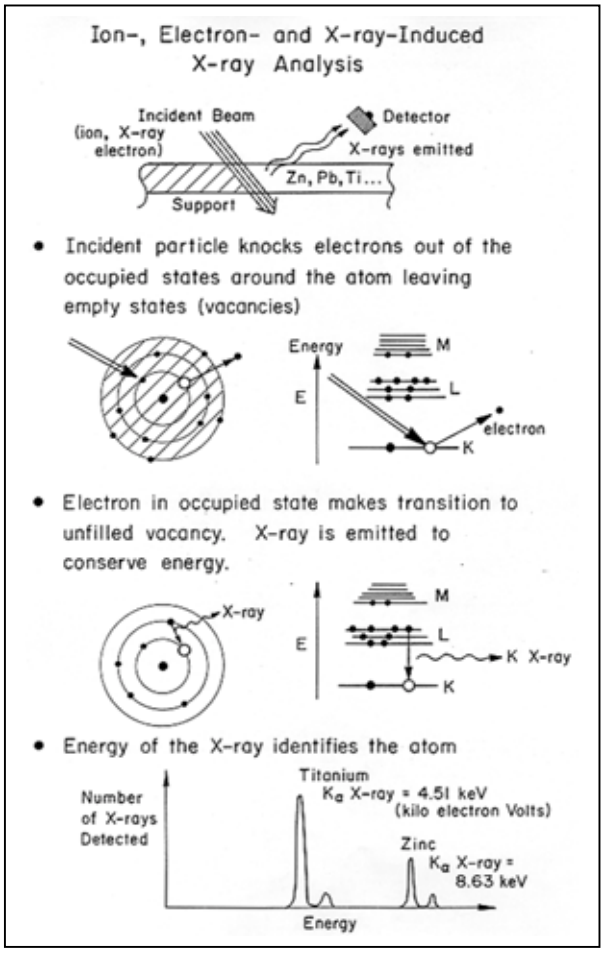
Modern Atomic Spectrometries: XRF, PIXE and RBS

I. X-Ray Fluorescence Spectrometry (XRF)

A. Description of Technique

X-ray fluorescence spectrometry (XRF) is a nondestructive method for the elemental analysis of solids and liquids using a x-ray beam. The sample is irradiated which causes the emission of fluorescent x-rays to emerge from the sample. The x-rays are collected and displayed in a spectrum with either an energy dispersive or wavelength dispersive detector. The elements in the sample are identified by the wavelengths (qualitative) of the emitted x-rays while the concentrations of the elements are determined by the intensity of those x-rays (quantitative).XRF is a bulk analysis technique with the depth of sample analyzed varying from less than 1mm to 1cm depending on energy of the emitted x-ray and the sample composition. The elemental detection is from sodium to uranium.

B. Energy Levels



1. K and L Lines

The XRF spectra are primarily from transitions that occur after the loss o f a 1s or 2s electron. The n= 1, 2, 3, 4 levels are denoted as the K, L, M, N shells.

Transitions which fill in the K level are the highest energy, and are called "K Lines":

Initial State: $^2S_{1/2}$ (1s; n=1, l=0, j = 1/2)

K_α Lines are from the n=2 levels:

$K_{\alpha 1}$: Final State = $^2P_{1/2}$ ($2p^5$; n=2, l=1, j = 1/2)
$K_{\alpha 2}$: Final State = $^2P_{3/2}$ ($2p^5$; n=2, l=1, j = 3/2)

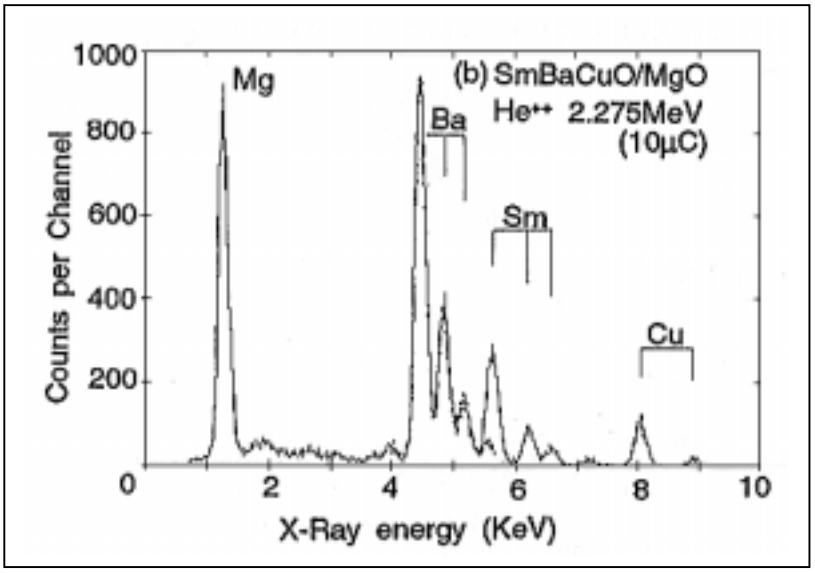
K_β lines leave a hole in the 3p shell, and K_γ lines leave a hole in the 4p shell.

Transitions which fill in the L level are called "L Lines":

Initial State: $^2S_{1/2}$ (2s; n=1, l=0, j = 1/2)
Final States leave holes in the 3p, 3d, (L_α) and 4p and 4d (L_β)shells.

2. Z Dependence of K and L Lines

The energy of the K and L lines increases with atomic mass Z. Since these transitions are so energetic, they do not vary much with oxidation state or chemical bonding of the element. Thus they can be used as an elemental analysis fingerprint spectrum. Note that this is quite different from AAS, which requires volatization into the gas phase.



C. X-Ray sources

1. X-ray tube
Accelerated electrons hit a target (typicaly W, Cr, Cu, Mo) that emits x-rays. Emission has two components -- a broad continuum (Bremsstrahlung), and K line spectra from the target element(s).

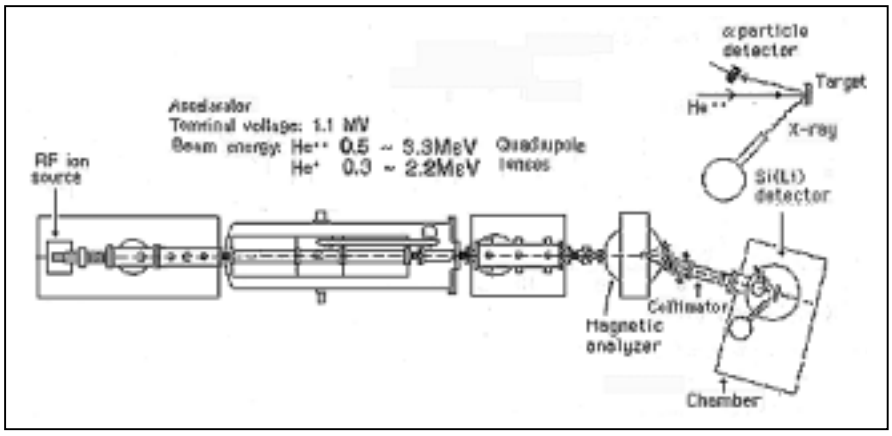
2. Radioactive Sources
Radioisotopes often emit X-rays after alpha particle emission, beta particle emission, or electron capture leaves a hole in a lower electronic shell. For example:

55Fe 54Mn + hν

K capture reaction that produce 5.9 keV X-Rays from Mn K Lines. This radioisotope has a half-life of 2.6 years.

Of course, no fluorescence can be observed for transitions with energies greater than the excitation source.

3. Particle Induced X-ray Emission (PIXE)
A third method of producing X-ray emission is to hit the sample with either an alpha particle or a proton. Since they are both charged, they can be accelerated to the target:



D. X-ray Detectors

Gas Filled Transducers: Geiger Tube, Proportional Counters are Ar filled tubes that produce ions and electrons with x-ray excitation

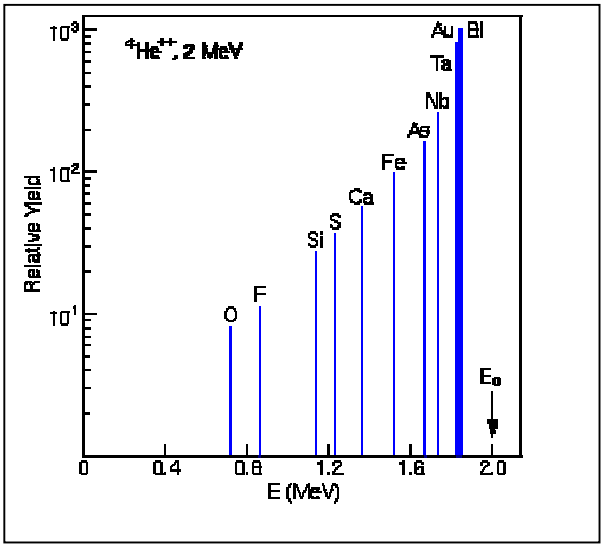
Scintillation Counters: NaI crystal that emits photons at 400 nm upon x-ray excitation

Semiconductor Transducers: Lithium-drifted Silicon "Si(Li)" detectors have Li-doped Si sandwiched inbetween a p-Si and n-Si junction. Highly energetic photoelectrons are produced in the Si(Li) region, which are proportionally converted to several thousand conduction band electrons.

To analyze the XRF, a spectrometer consisting of a collimator and a crystal can be used to separate the different x-ray wavelengths, but more typically, a pulse height analyzer is used to directly determine the energy of each incident photon. This way a spectrum can be generated without a monochromator, leading to a very compact instrument, esp. if a radioactive isotope source is used.

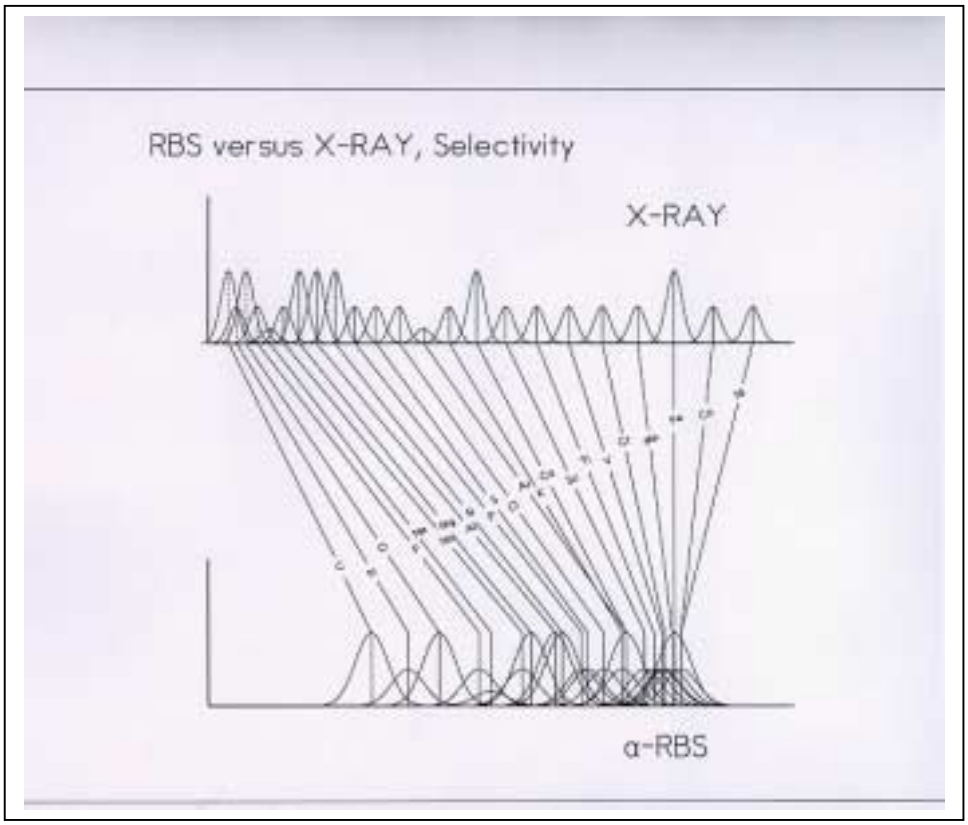
II. Rutherford Backscattering (RBS) Spectrometry

RBS measures the energy of alpha particles that are backscattered (180° scattering geometry) off of a sample. The amount of energy loss in the collision with the atomic nuclei depends upon Z:



Kinematic Theory. For scattering at the sample surface the only energy loss mechanism is momentum transfer to the target atom. The ratio of the projectile energy after a collision to the projectile energy before a collision is defined as the "kinematic factor." There is much greater separation between the energies of particles backscattered from light elements than from heavy elements, because a significant amount of momentum is transferred from the incident particle to a light target atom. As the mass of the target atom increases, less momentum is transferred to the target atom and the energy of the backscattered particle asymptotically approaches the incident particle energy. This means that RBS is more useful for distinguishing between two light elements than it is for distinguishing between two heavy elements. RBS has good mass resolution for light elements, but poor mass resolution for heavy elements. For example, when He++ strikes light elements such as C, N, or O, a significant fraction of the projectile's energy is transferred to the target atom and the energy recorded for that backscattering event is much lower than the energy of the beam. It is usually possible to resolve C from N or P from Si, even though these elements differ in mass by only about 1 amu.

An important related issue is that He will not scatter backwards from H or He atoms in a sample. Elements as light as or lighter than the projectile element will instead scatter at forward trajectories with significant energy. Thus, these elements cannot be detected using classical RBS.

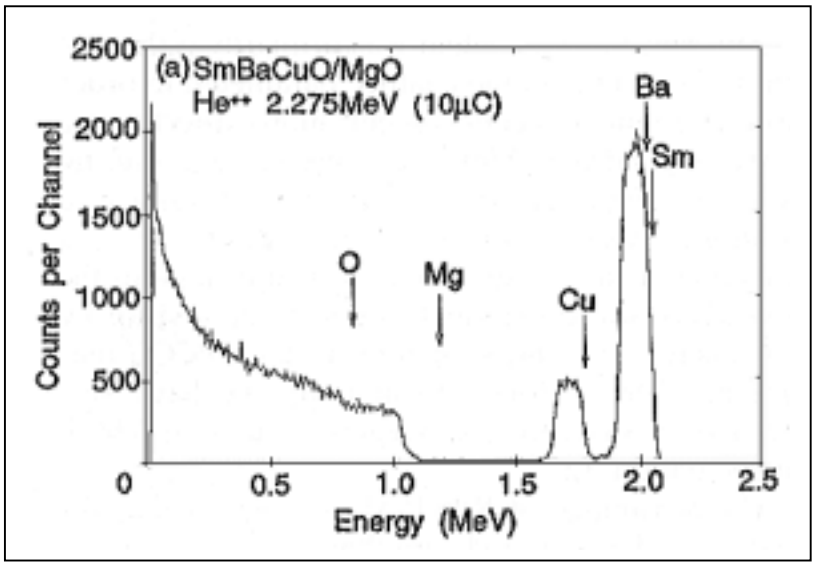


The good news is that this is exactly opposite of the selectivity of XRF. Therefore, if you use RBS in conjunction with XRF, you can cover virtually the entire periodic table.

Scattering Cross Sections. The relative number of particles backscattered from a target atom into a given solid angle for a given number of incident particles is related to the differential scattering cross section. The scattering cross section is basically proportional to the square of the atomic number of the target atom.

Stopping Power. Only a small fraction of the incident particles undergo a close encounter with an atomic nucleus and are backscattered out of the sample. The vast majority of the incident He atoms end up implanted in the sample. When probing particles penetrate to some depth in a dense medium, projectile energy dissipates due to interactions with electrons (electronic stopping) and to glancing collisions with the nuclei of target atoms (nuclear stopping). This means that a particle which backscatters from an element at some depth in a sample will have measurably less energy than a particle which backscatters from the same element on the sample surface. The amount of energy a projectile loses per distance traversed in a sample depends on the projectile, its velocity, the elements in the sample, and the density of the sample material. Typical energy losses for 2 MeV He range between 100 and 800 eV/nm. This energy loss dependence on sample composition and density enables RBS measurements of layer thicknesses, a process called depth profiling. RBS is therefore used as a Surface Analysis tool.

The majority of energy loss is caused by electronic stopping which behaves (roughly) like friction between the probing particles and the electron clouds of the target atoms. Nuclear stopping is caused by the large number of glancing collisions which occur along the path of the probing atom. Nuclear stopping contributes significant energy losses only at low particle energies. The ratio of energy loss to two-dimensional atom density for a given material is known as its stopping cross section (epsilon), commonly measured in units of eV-cm. Since the majority of energy loss is caused by interactions with electrons, the electronic structure of the target material has a significant affect upon its stopping power. Theoretical predications of stopping power are both complicated and inaccurate. Therefore, empirical stopping powers are often used in RBS calculations. A polynomial equation and a table of coefficients provides calculations of stopping powers over a wide range of energies and elements. In order to calculate the energy loss per unit of depth in a sample one can multiply stopping cross section times the density of the sample material (atoms/cm2). Sample densities can vary significantly. It is necessary to know the density of the sample material in order to calculate the depth of a feature or the thickness of a layer by RBS.



III. The Alpha-Proton-X-ray Spectrometer (APXS)

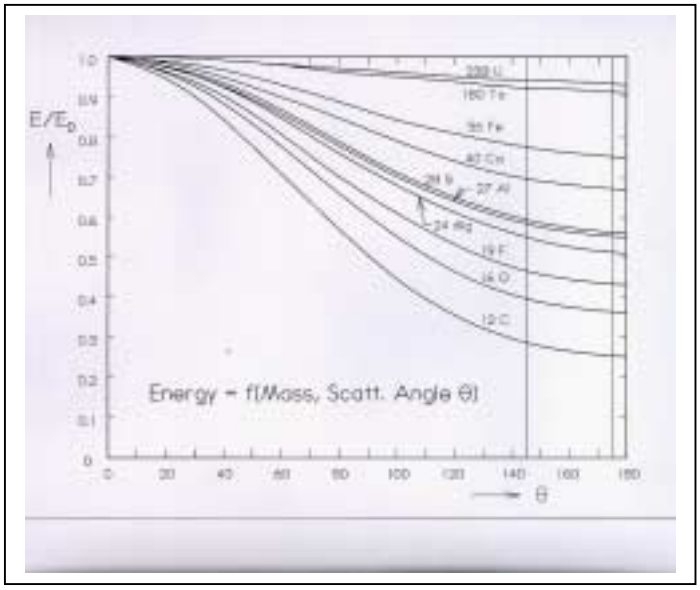
The Mars Pathfinder mission contained the consummate high energy elemental analysis measurement that was dubbed the APXS spectrometer. Here is a description from the designers of the instrument:

A. Overall Description

The Alpha-Proton-X-ray Spectrometer (APXS) for the Mars Pathfinder mission is designed to provide a complete and detailed chemical elemental analysis of Martian soil and rocks near the landing site. The APXS instrument is carried on the Pathfinder microrover, which will provide transportation to places of interest on the Martian surface. It consists of a complex sensor head, mounted on a simple, but sophisticated deployment mechanism (ADM) outside the Warm Electronics Box of the microrover (WEB), and the instrument electronics, mounted inside the WEB. The ADM permits to place the instrument sensor head against soil and rock samples in

arbitrary positions, ranging from horizontal to vertical, in order to perform in-situ analysis. The possibility to transport the APXS to an arbitrary location, pre-selected on Earth, and to perform in-situ analysis at it, constitutes one of the most exciting aspects of the Pathfinder mission. The principle of the APXS technique is based on three interaction of alpha particles from a radioisotope source with matter : (a) simple Rutherford backscattering, (b) production of protons from (a,p) reactions on light elements, and (c) generation of characteristic X-rays upon recombination of atomic shell vacancies created by alpha bombardment. Measurement of the intensities and energy distributions of these three components yields information on the elemental chemical composition of the sample. In terms of sensitivity and selectivity, data are partly redundant and partly complementary: Alpha backscattering is superior for light elements (C, O), while proton emission is mainly sensitive to Na, Mg, Al, Si, S, and X-ray emission is more sensitive to heavier elements (Na to Fe and beyond). A combination of all three measurements enables determination of all elements (with the exception of H) present at concentration levels above typically a fraction of one percent.

A.1 Alpha Backscattering (Alpha Mode)
Elastic collisions between alpha particles and atoms of a target (sample) material lead to a change in direction and energy of these particles. This process was first described by Rutherford in 1911 and is since then referred to as "Rutherford Scattering" (Rutherford, 1911). The energy E of a scattered alpha-particle, in relation to its initial energy E0 is a function of the mass A of the target atom and the scattering angle f:



In the case of a thick sample, alpha particles will be scattered at various depth along their path. Before scattering they will have lost energy in the sample and the scattered particle will lose additional energy on its way out of the sample. The resulting energy distribution is a - generally - flat spectrum, extending from 0 to a sharp cutoff at a maximum energy determined by E / E0 which is characteristic for the scattering element. The total number of particles registered in the spectrum is a measure for the number of atoms of the scattering element in the sample, i.e. its

concentration in the sample. These two facts are the basis for analytical applications of alpha backscattering.

A.2 Proton Emission (Proton Mode)
Another process important for analytical applications is the nuclear (a,p) reaction: Alpha particles merge with the target nucleus, followed by the emission of a proton and - in some cases - gamma radiation. This process is characterized by the Q-value, i.e. the difference in binding energy of the alpha-particle and the target nucleus on the one side and of the proton and the product nucleus on the other side. This process is energetically possible, when the kinetic energy of the incoming alpha-particle E exceeds the difference in binding energy Q; the excess energy is transferred to the kinetic energy of the proton Ep and the energy of an associated gamma transition Eg:

$$Ep + Eg = E + Q$$

This process is of particular interest in the case of the light rock-forming elements Na, Mg, Al and Si, where Q-values range between -2 MeV and +2 MeV and the reaction cross sections for alpha-particles of 5 to 6 MeV are not too small. This is due to the fact that alpha-particles have to penetrate the Coulomb barrier of the nucleus, before the nuclear reaction can take place, and this is determined by the nuclear charge of the target nucleus. Table 1 shows the Q-values for some selected target nuclei.

A.3 X-ray Generation (X-ray Mode)
The alpha particles from the radiation sources used in the alpha and proton modes are also used as a very efficient excitation source for production of characteristic X-rays from the sample material. Actually, charged particle excitation is preferred to any other kind of excitation since it produces the best signal-to-noise ratio due to absence of any Compton scattering. This advantage significantly improves the performance of the instrument. The addition of a small X-ray detector and only some additional electronics results in a significant extension of the accuracy and sensitivity of the Alpha - Proton instrument, particularly for the heavier, less abundant elements.

B. APXS Sensor Head
The sensor head contains nine 244Cm sources in a ring-type geometry and three detectors for the measurement of the three components: A telescope of two Si-detectors for the measurement of alpha-particles and protons and a Si-PIN X-ray detector with its preamplifier.

B.1 244Cm Alpha Radioactive Sources
The APXS needs for its operation in alpha, proton and X-ray modes a beam of alpha particles with high intensity and low energy spread: Intensity of the beam determines the total measurement time needed to obtain data with the necessary statistical accuracy; its energy spread directly determines the resolving capability of the alpha mode. For space applications, such a beam is most conveniently obtained from a radioactive source. In this case, however, intensity and energy spread are linked together and a suitable compromise has to be met: Given a finite source area, the intensity is determined by the amount of source material, i.e. its thickness, and its specific activity (determined by its half-life). On the other hand, alpha particles, emitted from within a thick source, loose energy on their path through the source material. Thus, thick sources

exhibit an inherent energy spread. It is therefore desirable to use radioisotopes with a short half-life, i.e. with high specific activity. In practice, the time between preparation of the source and its use sets a limit to the minimum useful half-life. 244Cm with a half-life of 18.1 years was chosen as suitable for applications on Mars.

Another important factor, determining the resulting energy spread of a source, is the chemical composition of the source material: Ideally one would use the source material in elemental form. In the case of curium such sources, however, tend to be chemically unstable and to rapidly deteriorate. In the past ten years an extensive research program has been undertaken by S. Ryadchenko et. al. at the Research Institute for Atomic Reactors in Dimitrovgrad, Russia, in search of suitable chemical forms for high quality sources. Intermetallic compounds with various metals (Pt, Ir, Rh, Pd) have been investigated and yielded promising results. More recent work concentrated on the formation of curium silicides on semiconductor grade silicon. This technology has yielded the best results so far and sources for the current Martian projects are manufactured by this technique.

B.2 Alpha-Proton Detector System:
The maximum energy in the backscatter spectrum of 244Cm is the emission energy of 244Cm , i.e. 5.80 MeV. A Si-detector of 35 mm thickness (D1) will completely stop alpha particles of 6.5 MeV, which means that there is a sufficient reserve for range straggling and partial channeling such that no backscattered alpha particle will penetrate this detector. On the other hand, this detector will become transparent for protons of an energy greater than 1.6 MeV. A second detector (D2) behind the 35 mm detector, thick enough to completely stop protons of energies up to 6 MeV (> 320 mm) will register these protons and the sum of the signals from both detectors will correspond to the total proton energy. With the help of threshold discriminators and a coincidence logic, events caused by alpha particles can be distinguished from events caused by protons and thus alpha spectra and proton spectra can be recorded separately. Figure 6a shows the energy deposited in the thin detector D1 and the thick detector D2 by protons, emitted from the sample. Using threshold settings are 0.4 MeV for both detectors, proton events can be distinguished from alpha events, if the proton energy lies between about 1.8 MeV and 6 MeV. Protons with an energy of less than 1.8 MeV are registered as alpha events. In practice, this is not critical, because (I) the significant part of the proton spectra is contained in the energy range above ~ 2 MeV and (ii) proton-events occur at a significantly lower rate than alpha events such that the alpha spectra are not noticeably disturbed by the presence of low energy protons.

The thick detector D2 plays a second important role as an active anticoincidence shield against cosmic ray protons. A proper choice of its thickness permits to suppress such events in the data evaluation, partly based on coincidence conditions and partly on the amplitude of the signals. Figure 6b shows the energies deposited by cosmic ray protons first striking a detector of 700 mm thickness (D2) and subsequently a detector of 35 mm thickness (D1). As can be seen from the figure, protons with an energy of less than ~ 9.8 MeV are completely stopped in the thick detector. Protons with energies above 9.8 MeV will also deposit energy in the thin detector. However, either the sum of the signals from both detectors is larger than the range of interest (6 MeV) or the signal in the thin detector is too small to exceed the threshold of the discriminator (0.4 MeV). A signal, only recorded by the thick detector, is discarded as an unwanted cosmic ray background event.

The above described detector arrangement ("telescope") requires that detector D1 is fully depleted, i.e. its "active" thickness is essentially identical with its physical thickness. The rear detector D2 must have an active thickness of at least 700 mm. Full depletion is not mandatory for this detector. However, the dead layer on the side facing detector D1, should be as thin as possible. The detectors must be mounted as close together as possible to minimize the solid angle, under which particles can arrive at D1 without passing through D2.

B.3 Description of the X-ray sensor head

The X-ray mode of the APXS uses solid state X-ray detectors, which are the result of the latest technology development. They operate at or slightly below room temperature. The elimination of the cryogenic resources and any associated plumbing related to such a system enables an exceptional degree of miniaturization of the APXS instrument. Figure 7 shows schematically the arrangement of the X-ray detecting system and its components. It consist of the silicon PIN photodiode X-ray detector mounted on a beryllia substrate on top of the cold side of a Peltier cooler, the front end of a charge sensitive preamplifier, and, a temperature sensor. All these components are enclosed in a hermetically sealed metal container the size of a TO-8 can, filled with inert gas (made by AMPTEK corporation). A thin (8 micron) beryllium window in the front enables entry even for very low energy X-rays into the detector system. An important part of the system is a tungsten ("heavy met") collimator inside the hermetically sealed container. Its purpose is twofold: It collimates the X-ray detector, so it analyzes the same sample area as the alpha and proton detectors, and, at the same time it shields the detector from the X-rays and other gamma-rays coming directly from the alpha radioactive sources that due to tight geometry are very close to the X-ray detector. The small Peltier cooler, consuming about one watt of electrical power, is very convenient during laboratory testing, final integration and environmental testing on board the spacecraft. For this purpose it is powered from a D-size 1.5 V battery that lasts for about 6 hours of continuous operation. It will not be needed during the operations on the surface of Mars.

The output from the fist stage of the preamplifier is fed into the charge sensitive preamplifier sitting on the top of the sensor head. Since the preamplifier is not inside the temperature controlled compartment, its temperature will be in equilibrium with Martian ambient temperature in the range of -100 C to +10º C. The preamplifier was designed for proper operation at the Martian temperature range. It was tested and operated down to a temperature of -120º C.