

Multielemental Analysis Using Proton Induced Photon Emission

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Energetic protons from a nuclear accelerator can be used to provide quantitative analysis for most elements from Li to Pu. The sample is prepared as a thin film and bombarded with protons to produce monoenergetic x rays and γ rays from all elements in the sample. Energy sensitive Si-Li and Ge-Li semiconductor devices are used to detect x rays and γ rays, respectively. The energy of the radiation identifies the element and the intensity determines the concentration of the element in the sample. A PDP 15/45 on-line computer is used to process data from one sample while data is being accumulated from the next sample. The analysis results are available from the computer at approximately the same time that new data accumulation is finished.

Proton excitation provides better sensitivity than electron excitation because the yield of characteristic x rays compared to background radiation is higher. Protons have an advantage over x-ray excitation because good sensitivity can be obtained for a much larger group of elements in a single measurement. In addition, the light elements Li, B, F, Na, Mg, Al, and Si can be detected by γ -ray emission following nuclear excitation.

The broad elemental range of Proton Induced X-ray Emission (PIXE) occurs because the production of characteristic x rays is very large in the energy region where the background radiation is maximum. The primary source of background radiation comes from showers of electrons which are released when a proton strikes the target. These electrons stop in the target and produce a continuous x-ray spectrum called Bremsstrahlung or braking radiation. The Bremsstrahlung intensity decreases rapidly as a function of energy and is essentially negligible above 10 keV for 4 MeV incident protons. The background at higher energy is primarily due to nuclear γ rays which occasionally interact with the x-ray detector. The probability for K x-ray emission also decreases with the atomic number of the element, but the x ray yield is still satisfactory up to the rare-earth elements because the background is so small. Elements heavier than La are detected by L x rays. The L x-ray yields for the rare-earths are good but their energy falls in the region of relatively high Bremsstrahlung so the sensitivity is poorer than for other regions. For heavier elements the L x rays occur above the Bremsstrahlung so the sensitivity is again excellent. The background in the γ -ray detector depends on the major components in the sample. For example, large quantities of Na or Cu in the sample can produce relatively intense γ -ray background.

Sample preparation. Solid samples are usually ground to a fine powder using Agate components in a vibrating mill or a mortar and pestle. A few milligrams of the fine powder is placed on a thin plastic film (2.5×10^{-3} mm thick) and weighed with a micro-balance. A few drops of liquid plastic are added and the sample is stirred with a plastic rod to make a uniform suspension of the fine powder. When the plastic solvent evaporates, the sample is firmly attached to the backing in a light weight matrix. The sample uniformly covers a 16 mm diameter circle. The plastic film with sample is mounted in a 35 mm photography slide frame. The sample is not damaged in the bombardment so it can also be studied with other techniques. Thin samples are preferable to minimize x-ray absorption and to avoid corrections due to slowing down of the protons in the sample. However, thick solid samples can be analyzed with slightly poorer sensitivity and accuracy. Materials desolved in an aqueous sample can also be deposited on thin films for analysis.

Target bombardment chamber. The proton beam passes through a 2.5×10^{-3} mm Al foil located 3 meters in front of the target to diffuse the beam and ensure that

the proton bombardment is uniform over the target area. The beam is restricted with a series of collimators to ensure that the protons can only strike the sample and the thin support film. Carbon or plastic films are used to cover all metal parts of the chamber that might be struck by protons scattered from or passing through the target. Bombardments are performed in vacuum. Eighty targets are held in the circular slide tray of a modified 35 mm slide projector. The target to be bombarded is dropped into the proton beam by the automatic mechanism of the projector. A variety of filters can be inserted between the target and the detector by remote control to reduce the intensity of abundant x rays which would interfere with the analysis of trace elements. The x rays pass through a 0.025 mm plastic window on the target chamber and a 0.025 mm Be window on the detector cryostat.

Detector and electronics. A Si-Li detector (1 cm diameter and 3 mm thick) provides 170 eV energy resolution for 5.9 keV x rays. A 40 cm^3 Ge-Li detector provides 2.0 keV resolution for 1.33 MeV γ rays. Normally when an x ray is absorbed in the detector, all of the x-ray energy is converted into an electrical pulse. However it is also possible for a Si x ray, created in the detection process, to escape from the detector. These "silicon escape" events create false peaks in the x-ray spectrum. It is also possible for electrons released in the detector process to leave the surface of the detector. These events produce a small tail on the low energy side of peaks in the x-ray spectrum. The computer must be able to correct for these two imperfections in the detector response in order to get accurate analytical results.

The electrical signal from the detector is amplified and passed through a noise filter which is essential for good energy resolution. Fifty microseconds are required for the noise filter to process each x ray pulse. If a second x ray is detected while the filter still contains a preceding x ray, the energy of both x rays is distorted. This problem is greatly reduced in our system by switching the proton beam off of the target shortly after the first x ray is detected. As soon as the noise filter has processed the x ray pulse, the beam is automatically returned to the target to produce a new x ray.

Even though the beam switching time is less than $0.5\ \mu\text{sec}$, there is still a small probability that a second x ray will be produced before the beam is removed from the target. When two x ray pulses pile up in the filter a single pulse is produced which corresponds to the sum of the energy of the two x rays. We have developed a circuit which recognizes pile-up events and rejects them unless the second x ray is emitted within $0.05\ \mu\text{sec}$ of the first x ray. These remaining "simultaneous" pile-up events are rare, so they usually do not present a significant limit on the analysis.

The task of separating events which come from two x rays of similar energy is greatly simplified if the energy calibration of the electronic system is very stable. The energy calibration is always a function of the counting rate in the detector. Our system has correction circuits (Kevex Model 4532P Pulse Processor) which limit the calibration variation to less than 0.01% for counting rates up to 10^4 x rays per second.

The proton beam is collimated so that all protons which enter the target chamber must pass through the target. The total charge which is accumulated in the chamber during a measurement is recorded by a digital current integrator (Ortec Model 439) and stored in the computer. The quantity of charge on each proton is well known, so the computer converts the total charge into number of protons passing through the sample. The computer also corrects for the number of events lost due to pile-up (typically less than 3%).

Computer processing. The analysis process is monitored and the computer is controlled with an interactive video display. The first step in the analysis process is to subtract background radiation. Many experimental background spectrum are stored on a magnetic disk. The operator selects a background spectrum which represents the host material of the target being analyzed. The computer adjusts the background to match the target including the effect of the peak-tails described above. The background is then displayed on the video monitor as an overlay on the experimental data. Usually, the computer generated background accurately describes the actual background from the sample, but the operator can instruct the computer to refine the background by contacting the display with a "light pen".

The computer also has stored experimental data which describe the shape and the position of the characteristic x-ray peaks in the spectrum. Even though the imperfections in the detector response are small, they can be important for large peaks. The computer locates large peaks and identifies their tails and the false peaks that are produced by Si-escape x rays. Very large peaks can also produce false peaks due to simultaneous pile-up. The computer includes these refinements and performs a least square fit to the data to determine the number of x rays at each energy of interest. The stability of the energy calibration, the advanced knowledge of the shape of the characteristic x-ray peaks, and the careful treatment of imperfections and false peaks are all essential factors for accurate analytical results.

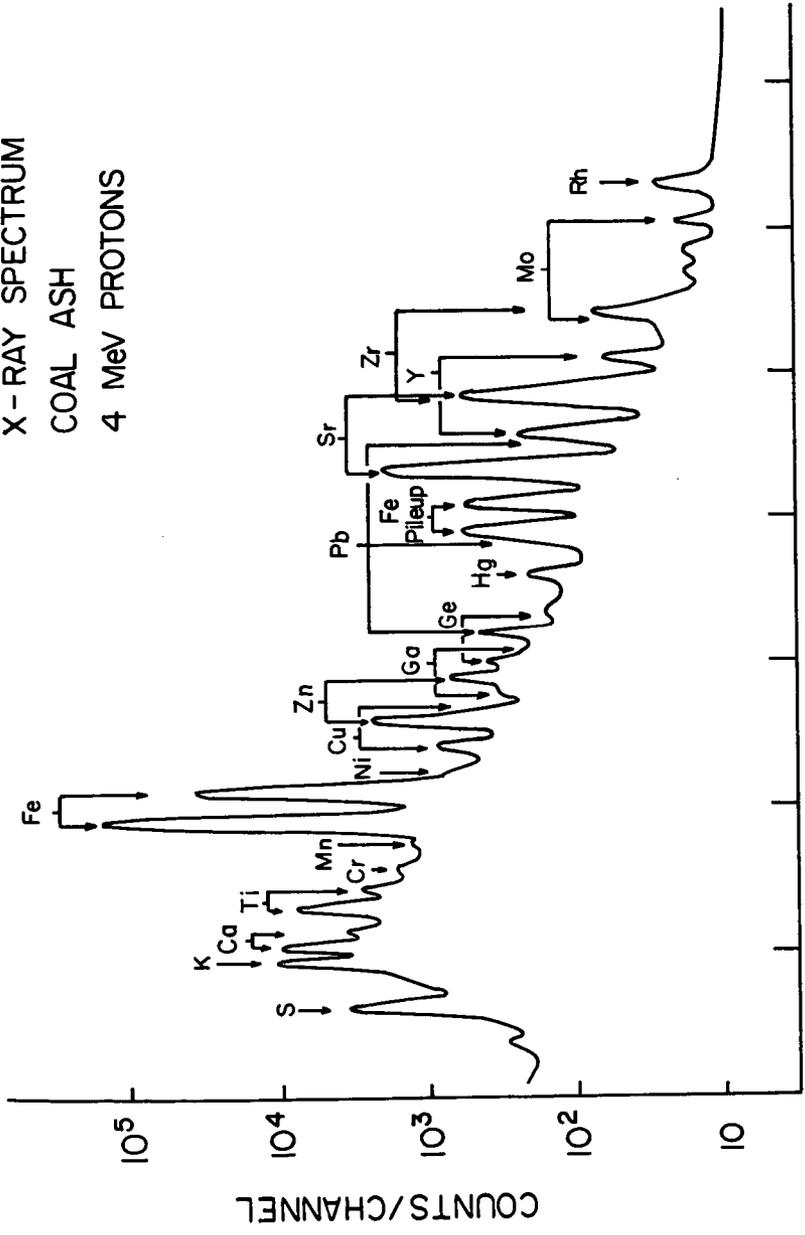
A typical spectrum for the lower energy portion of a coal ash sample is shown in Figure 1. The results of the computer fit is displayed on the video monitor as an overlay on the data. The operator can easily recognize any element which has been missed or incorrectly inserted and instruct the computer with the light pen to refine the fit to the data.

Most elements emit two or more x rays (for example, notice the two peaks from Sr identified in Figure 1). The relative heights of these peaks have all been measured experimentally for single element calibration targets. The computer checks that the fit to the sample data agrees with these standards. The computer also looks for possible sources of error due to two x rays which have approximately the same energy. All of this information is printed out for the operator to evaluate the reliability of the analysis.

After the operator has approved the analysis of a sample, the computer uses the number of protons passed through the target and stored calibration tables for the proton energy and filter conditions to determine the weight of each element in the sample. These weights are divided by the total sample weight to calculate the fractional weight of each element.

System calibration. The basic relation which must be known to obtain analytic results is the number of x rays detected, per unit of protons, per unit of weight of the element. This x-ray yield has been measured for a fixed detector position, for each proton energy, and each filter condition. Thin film calibrators (typically 100 μ grams/cm²) are used so that it is not necessary to correct for slowing down of the protons or x-ray absorption in the calibrators. Thirty metal films of known weight deposited on Mylar were obtained from Micromater Inc. Thirty five calibrators were made in our laboratory from commercial atomic absorption liquid standards. The x-ray yield is a slowly varying function of atomic number. The results of yield measurements for each proton energy and filter condition were least square fit to an algebraic function to obtain yield curves for all elements from Al to Pu. The RMS deviation of the individual measurements around the best-fit function was typically 3%. Gamma-ray yields were measured for each light element that is detected by γ rays.

X-RAY SPECTRUM
 COAL ASH
 4 MeV PROTONS



Limitations to analysis. As noted above the x-ray counting rate is limited by the noise filter which is essential for good energy resolution. Thus the number of x rays that can be observed from trace elements in a fixed time period will be limited by intense radiation from an abundant element. Analysis cost are directly effected by bombardment time, so the most practical solution is to reduce the intensity of the dominant radiation with an absorber. Energy selective filters can be useful for special problems, but the best general technique is to select a material where the probability of absorption decreases rapidly with increasing energy. The unwanted x ray can be controlled, but all lower energy x rays will be lost. However, higher energy x rays will be retained with minimum loss. Carbon is a good filter material and it is conveniently available in thin plastic films.

For coal samples we detect all elements heavier than Fe with 4 MeV protons and a 5 mm thick plastic filter to absorb Fe x rays. Elements from Al to Fe are observed in a separate measurement with 2.5 MeV protons. There is some x-ray absorption due to the windows which separate the target and detector. It would not be desirable to eliminate these windows because they prevent scattered protons from reaching the x-ray detector. The high intensity x rays from Fe and S in coal limit the data rate that can be obtained for light elements. However, light elements are frequently relatively abundant and their x-ray yields are large so good results can be obtained for most elements.

In some cases an intense x ray from an abundant element or a false peak due to simultaneous pile-up will have approximately the same energy as a low intensity x ray from a trace element. Then the sensitivity for that trace element will be limited to a fraction of the abundant element. These limitations are predictable so they can be included in the specifications for PIXE analysis.

Detection limits. The sensitivity is determined primarily by the time that the target is exposed to the proton beam. Other significant factors are background radiation, the presence of elements in high concentration, and energy interference for a few elements. The detection limit is relatively poor for P (approximately 250 ppm) but it rapidly improves to approximately 2 ppm for Cr, Mn, and Fe. The detection limit is approximately 1 ppm for most elements from Co to I, approximately 10 ppm for the rare-earth elements, and typically 3 ppm for the heavy metals up to Pu. The detection limit using γ rays for the light elements Li, B, F, Na, Mg, Al, and Si is usually a few ppm.

Results obtained for the analysis of NBS standard reference material 1632 (coal) are given in Table 1. The cost for this type of analysis would be \$30 to \$80 per sample depending on the number of samples that were analyzed.

In summary, PIXE is a powerful technique for multielemental analysis of a wide variety of samples. Very light elements can be observed by detecting γ rays and x rays in the same experiment. Although the original cost of the equipment is very large, there are many laboratories which already have the required facilities. After the system is developed the cost of analysis is low compared to other multielemental techniques of comparable sensitivity.

Table 1
 Analysis of NBS Standard Reference Material 1632 (Coal) by PIXE
 Results given in parts per million by weight

Element	Purdue PIXE		NBS Value	
	N Result	ΔN Uncertainty	N	ΔN
Al	17600	1500		
Si	34000	4000	32000	
S	11300	1000		
Cl	850	80		
K	2540	250		
Ca	3500	300		
Ti	890	90	800	
V	35	3	35	3
Cr	17	3	20.2	.5
Mn	36	3	40	3
Fe	7900	800	8700	300
Co	10	6	6	
Ni	15.6	1.5	15	1
Cu	16	1.5	18	2
Zn	33	3	37	4
Ga	5.3	0.5		
Ge	2.4	0.3		
As	5.0	1	5.9	.6
Se	3.0	.3	2.9	.3
Br	20.5	1		
Rb	18.9	1		
Sr	140	10		
Y	7.5	.5		
Zr	35.5	1.5		
Nb	2.2	0.5		
Mo	2.2	0.5		
Ag		$\leq .3$		≤ 0.1
Cd	0.5	0.3	.19	.03
Sb	3.0	1		
Ba	310	30		
La	15	5		
Hg		< 1	.12	.02
Pb	23	4	30	9
Th	3.7	1	3.0	
U	2.1	1	1.4	.1