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G. S. Bench, A. J. Antolak, D. H. Morse. D. W. Heikkinen, A. E. Pontau,
R. B. James, D. C. David, A. Burger, and L. Van den Berg

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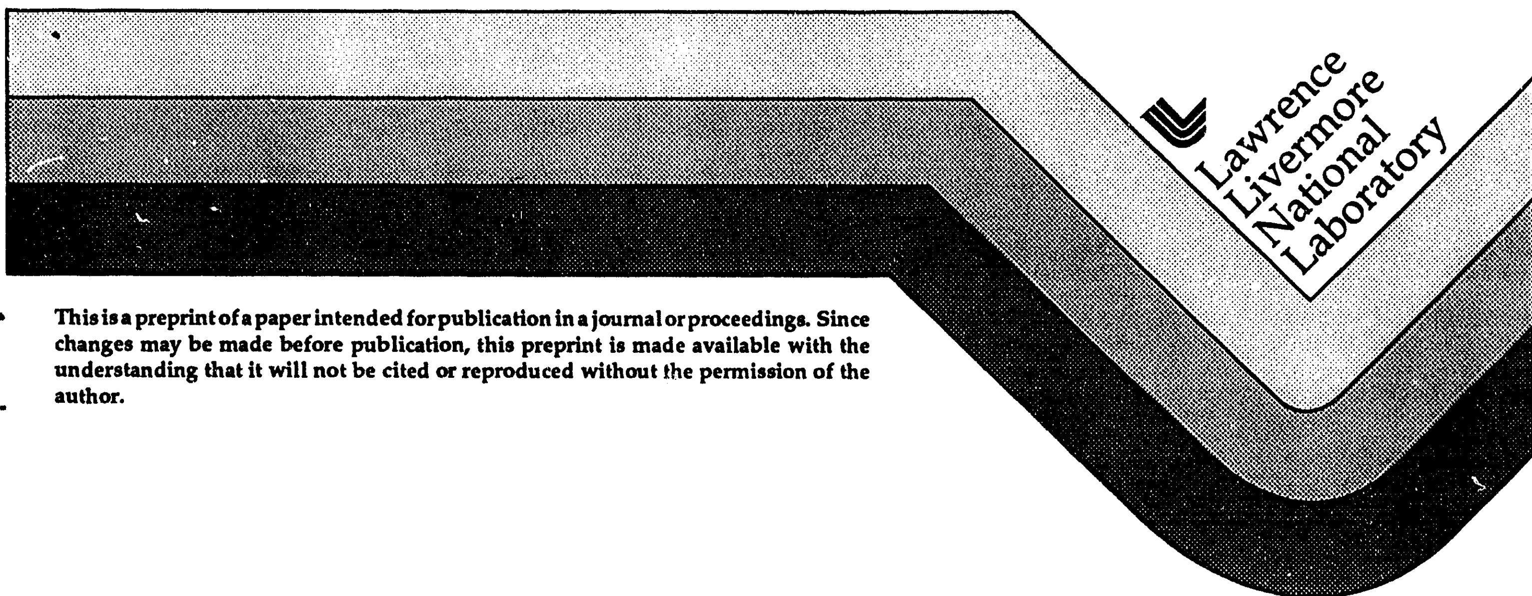


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# ANALYSIS OF $HgI_2$ AND $PbI_2$ CRYSTALS AND DETECTORS BY PARTICLE-INDUCED X-RAY EMISSION (PIXE) AND ION BACKSCATTERING SPECTROSCOPY (IBS)

G. S. BENCH[†], A. J. ANTOLAK[§], D. H. MORSE[§], D. W. HEIKKINEN[†], A. E. PONTAU[§], R. B. JAMES[§], D. C. DAVID[§], A. BURGER[•], and L. VAN DEN BERG[+]
[†]Lawrence Livermore National Laboratory, Livermore, CA 94550
[§]Sandia National Laboratories, Livermore, CA 94551
[•]Fisk University, Nashville, TN 37208
[+]EG&G Energy Measurements, Goleta, CA 93116

## ABSTRACT

The Ion Micro-Analysis Group (IMAG) in Livermore conducts quantitative trace elemental analysis with PIXE and depth profiling with IBS using an MeV ion microbeam. The system has the capability to produce two-dimensional trace element and IBS images. PIXE analyses have been conducted on $HgI_2$ and $PbI_2$ crystals and detector materials in order to identify and quantify near surface trace contaminants. IBS measurements have been conducted to investigate elemental depth distributions in various materials. The results of measurements on several different samples are reported and a discussion of factors affecting quantitative *in vacuo* microanalysis of these materials is presented.

## INTRODUCTION

The Ion Micro-Analysis Group (IMAG) in Livermore is an integrated group of scientists and engineers who use accelerator-based techniques to provide nondestructive materials characterization. Two of these techniques, pa :le-induced x-ray emission (PIXE) and ion backscattering spectrometry (IBS), are particularly useful for studies of near-surface impurity profiles, diffusion-mediated reactions, or minor and trace element compositions [1, 2]

PIXE's sensitivity for trace element detection is on the order of a few parts per million. When ions pass through matter, they interact with the electrons in the atoms producing vacancies. In an inner shell, the created vacancy can be filled by an electron from an outer shell and an x-ray photon of characteristic energy can be emitted. By measuring the photon energy, the element from which the x ray orginated can be determined and the amount of that element present can be determined from the number of x rays generated. For identification and quantification of trace elements, PIXE can be 100 times more sensitive than electron microanalysis due to the much reduced secondary electron bremsstrahlung background. Usually the measurements are made with protons, but heavier ions can be used to increase sensitivity in some instances since the cross section scales roughly as $Z^2$. IMAG has a dedicated PIXE beamline using 1-5 MeV/nucleon incident ions. The range of protons at these energies is between ten and a few hundred microns in $HgI_2$ so PIXE is primarily a tool for near surface analysis. Ions can be focused with a quadrupole lens system down to spot sizes of 10 $\mu$m at present. The ion beam can be rastered over the sample to provide two-dimensional spatial distributions of the elements. Characteristic x-rays are detected with a Si(Li) detector which has a resolution of 200 eV. The IMAG PIXE system uses approximately $10^{10}$ ions/s and data can be acquired simultaneously from elements with $Z \geq 11$ (typically a few minutes per spot). Final spectral data analysis is accomplished with a suite of IMAG-developed computer software.

High energy ion scattering is routinely used for obtaining elemental depth profiles. Utilizing the 10 MV tandem accelerator, IMAG has the capability to conduct ion backscattering spectroscopy (IBS) measurements with protons and high energy heavy ions. By measuring the energy of the recoiling ions, depth distributions of the elemental constituents can

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be determined which are useful for studying interfaces, thin films and multilayers. Quantitative data analysis is obtained using standard backscattering software on a computer workstation.

## EXPERIMENT AND ANALYSIS

$HgI_2$'s low sublimation energy requires that special sample preparation procedures must be followed before PIXE or IBS analysis can be done *in vacuo*. In order to minimize material removal under these conditions, samples are coated with a thin layer (< 5 μm) of either carbon or parylene. Use of this protective layer has enabled measurements to be made with current densities of up to 1 $\mu A/cm^2$ for 3-MeV protons with no observable damage to detector materials. Alternative methods such as using a cold stage in the analysis chamber or external beam techniques have not yet been fully explored. However, parylene coatings on $HgI_2$ are routinely used to encapsulate and protect fabricated detectors.

Figure 1 shows a typical 3-MeV PIXE spectrum from a 5 x 5 $mm^2$ $HgI_2$ detector-grade crystal which was partially covered by a 2 mm diameter thin contact layer of palladium. The sample was then coated by a 4 μm layer of parylene and then encased in a cadmium collar which exposed the contact layer. The beam spot was focused to a size of about 200 x 200 $\mu m^2$ and the spectrum was collected in 25 minutes. To attenuate the intense iodine L x rays, 0.76 mm of mylar was placed in front of the Si(Li) detector. Consequently, trace elements with atomic numbers less than 20 could not be detected in this experimental arrangement. The cadmium signal in the figure arises from the iodine K x rays fluorescing the cadmium collar.

**Figure 1.** PIXE spectrum from a $HgI_2$ detector-grade crystal covered by a thin contact layer of palladium. The characteristic x ray lines for elements are labeled.

Secondary fluorescence from the iodine also contributes about 10% to the palladium signal. The PIXE analysis revealed that the crystal's stoichiometry, Hg:I, was 1:2.2±0.3. The palladium layer thickness in the examined region was determined to be 90±20 Å after secondary fluorescence corrections were applied (the nominal value was 125 Å). Small amounts of iron, copper and nickel were also observed although secondary fluorescence of impurities in the cadmium collar is the dominant contribution to these signals. Spot analyses

made on other non-encased $HgI_2$ samples typically show iron, copper and nickel levels on the order of 100 ppm or less in the corresponding spectra. Inductively coupled plasma mass spectrometry has also shown the presence of these elements in $HgI_2$. PIXE data for a two-dimensional spatial map over the palladium contact were collected after the cadmium collar was removed from the sample. The 3-MeV proton beam spot size was 200 μm and the data were acquired in 200 μm steps. The average palladium contact layer thickness was determined to be 99±18 Å. Figure 2a shows the 4 x 4.4 $mm^2$ pixel image obtained by setting an energy window around the palladium K-line. The line of high (black pixels) concentration is a palladium wire leading to the circular contact. Although the distribution of iron appeared to be uniform across the scanned region, the copper distribution was non-uniform as shown in Figure 2b. The copper level in one region (dark pixels) is around 0.5 weight % while less than 40 ppm is detected in the.rest of the scanned area. Zinc is also present in the high copper containing region but is below detectable limits (20 ppm) in the rest of the scanned area.

**Figure 2.** Two-dimensional PIXE maps of (a) palladium and (b) copper from the same $HgI_2$ crystal of figure 1 but with the cadmium collar removed.

A possible mechanism affecting detector performance is the presence of impurities in the as-grown detector crystals due to the fabrication process. One method of initially removing impurities from these materials is called zone refining. In this technique, a heating element is passed several times across an ampoule containing the grown crystals resulting in reduced impurity levels near the center of the ampule. PIXE measurements were conducted on several zone refined $PbI_2$ samples taken from both ends of the ampoule and around its center. The analysis showed that iron, copper and nickel concentrations could be reduced (up to 20% ) near the ampule center.

Other possible means of introducing impurities into the crystals can be diffusion or electromigration of contaminants originating from the contact material. IMAG has conducted extensive PIXE and IBS measurements on several samples in order to identify and quantify trace elements in contact materials. Figure 3 shows a 3-MeV PIXE spectrum from a self-supporting piece of a water-based hydrocarbon gel (hydrogel) commonly used as an electrical contact for photodetector applications. In this analysis, a 150 μm beryllium filter was placed in front of the detector to prevent backscattered ions from penetrating into the Si(Li) crystal.

Consequently, only elements with atomic number greater than 12 were detectable. The impurities identified in this material were sulphur at a concentration of approximately 11 g/kg and silicon at 5.3 g/kg. However, in other plastic-type contact materials concentrations of

**Figure 3.** A PIXE spectrum from a self-supporting hydrogel sample. The x ray lines for silicon and sulphur are identified.

**Figure 4.** A backscattering spectrum from a 3-MeV proton beam incident on a hydrogel sample. The surface energies of several elements are shown.

sodium up to 20 g/kg, chlorine to 20 g/kg, iron to 3 mg/kg and zinc up to 100 mg/kg have also been observed. Figure 4 shows a 3-MeV proton IBS spectrum of a 2 mm thick hydrogel layer on a portion of a bare $HgI_2$ crystal. Backscattered particles were collected with a silicon surface barrier charged particle detector at a scattering angle of $120^o$. This sample had been stored for two years prior to analysis. In this case, the purpose was to determine whether Hg and/or I diffuse directly through the hydrogel or if $HgI_2$ outside the hydrogel contact sublimes and then redeposits on the outer surface of the hydrogel. At this beam energy, protons can only penetrate approximately 100 μm into the hydrogel. The surface energies of several elements are labeled n the figure. The two peaks between 2.9 and 3.0 MeV each have a FWHM equal to that of the
detector resolution. The position of the lower energy peak corresponds to the iodine surface energy, while the position of the higher energy peak corresponds to mercury's surface energy.

**Figure 5.** A backscattering spectrum from a 20-MeV oxygen beam incident on a thick $HgI_2$ sample. The surface energies of mercury and iodine are clearly separated.

These data indicate that the only detectable Hg and I exist as a thin film on the hydrogel and/or are distributed within the first 2.0 μm below the surface (2.0 μm is the approximate depth resolution of the experiment). The Hg:I atomic ratio is determined to be $1{:}2.1\pm0.2$. Consequently, it is most likely that the deposited Hg and I is caused by sublimation from the exposed parts of the crystal. This assumption gives a $HgI_2$ surface layer thickness of 10 Å. It should be noted that this surface layer may have formed during the time the sample was in vacuum in the analysis chamber. The chamber was at a pressure of approximately $10^{-5}$ torr and the measurements were made at room temperature. The sample was not protected by a thin carbon or parylene layer. Thus, these deposits could be caused by sublimation of the exposed $HgI_2$ while in vacuum. The backscattered spectrum in figure 4 also shows the presence of sodium, sulphur and possibly some chlorine in the hydrogel in addition to C, N and O. The data indicates that the sodium and sulphur have a uniform depth distribution in the analyzed region.

Owing to the light mass of the bombarding particle, an IBS spectra of 3-MeV protons on a bare $HgI_2$ crystal would produce a spectrum with the separation between the Hg and I surface energies of less than 100 keV. Quantitative information in this case can be very difficult to

extract. It is more advantageous to use heavier ions in order to obtain greater differences in kinematic factors for moderate- to high-Z elements. Figure 5 illustrates this fact by showing an IBS spectrum for a 20-MeV oxygen beam bombarding the same crystal. The spectrum was collected with the particle detector located at a 120$^{o}$ scattering angle. The mercury and iodine surface energies in figure 6 are separated by about 2 MeV and quantitative analysis of this spectrum yields a Hg:I ratio in the near surface of the sample as 1:2.04±0.09. Any other elements present were below minimum detection limits for this analysis. An additional advantage of using relatively low energy heavy ions is that the scattering cross section more closely follows conventional Rutherford scattering than does the analogous proton data. IMAG hopes to use such beams to study the diffusion and electromigration properties of elements such as palladium or silver into the near surface of $HgI_2$ materials.

## SUMMARY

The Ion Micro-Analysis Group (IMAG) has conducted preliminary PIXE and IBS measurements on $HgI_2$ and $PbI_2$ radiation sensor materials. These ion beam techniques are useful for studying near surface contaminants and elemental depth distributions. Problems related to the low sublimation energy of $HgI_2$ and performing the measurements in vacuum have been overcome by coating the crystals with thin layers of carbon or parylene. Various trace elements have been identified and are consistent with measurements made by other methods. In the future, IMAG will continue to analyze these materials with PIXE and IBS by focusing on the effects of diffusion and electromigration of contaminants. In addition, another ion microbeam technique, ion channeling, may be used to investigate crystalline structure and defects in these materials.

## ACKNOWLEDGEMENTS

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Figure 1

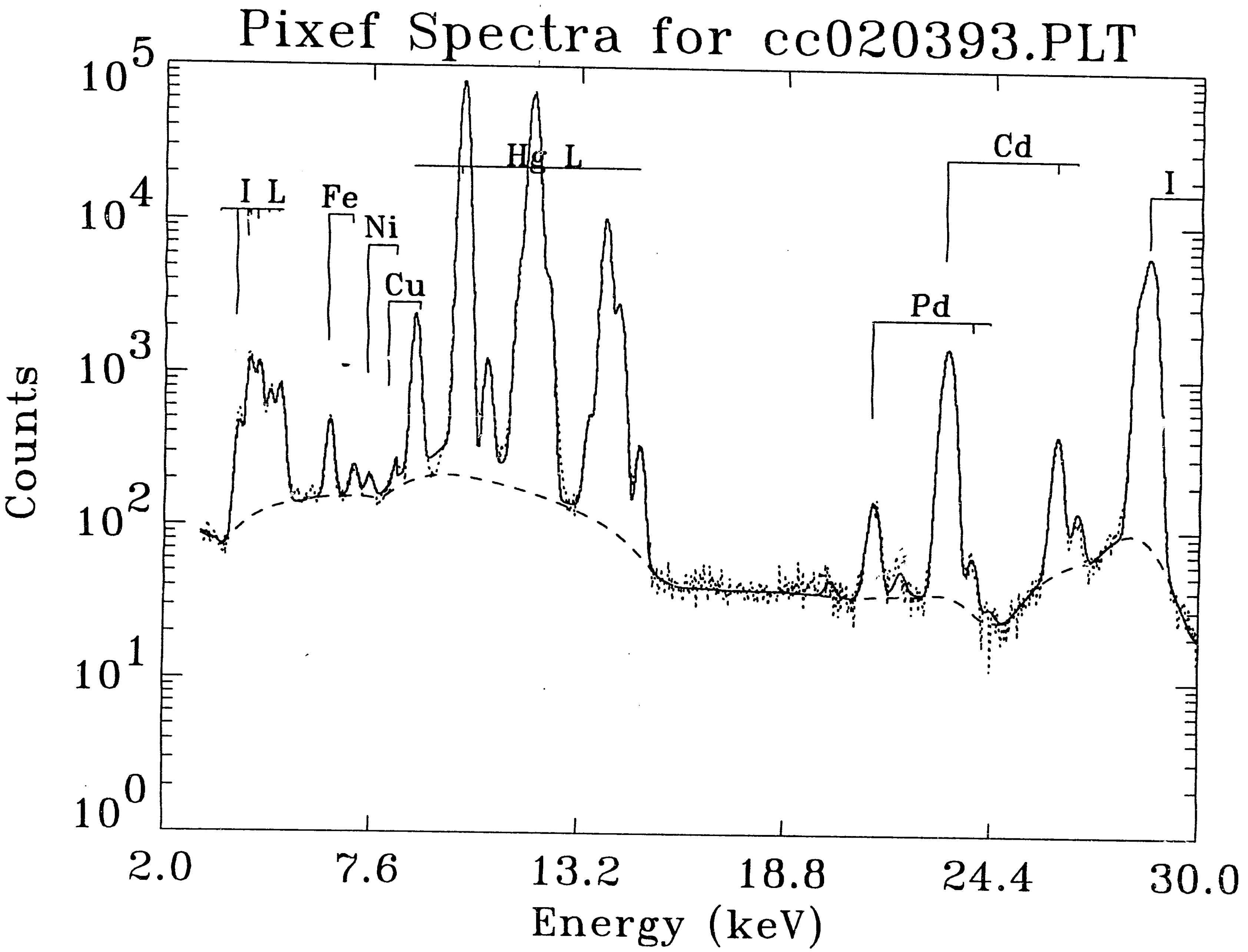
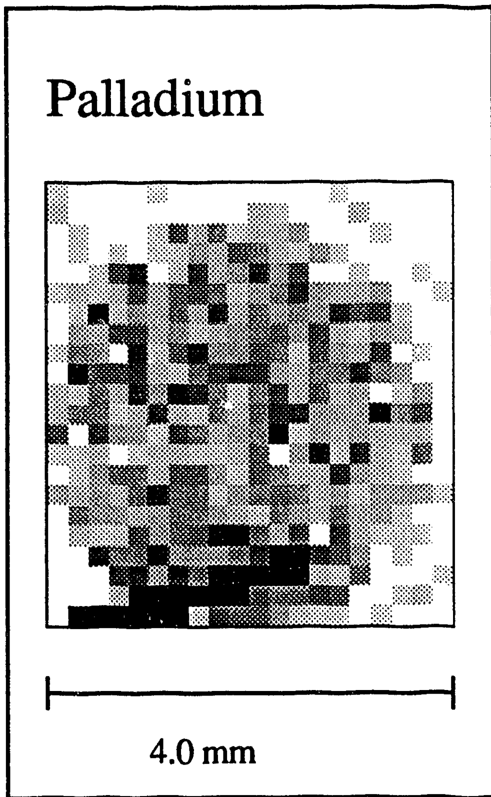
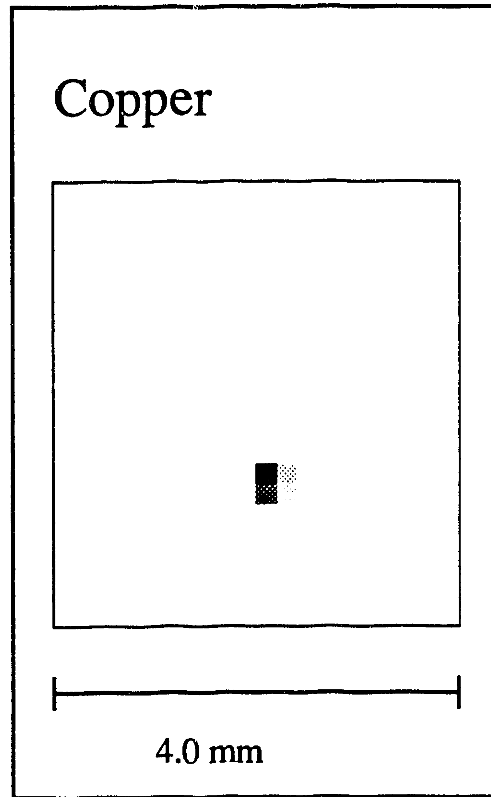


Figure 2



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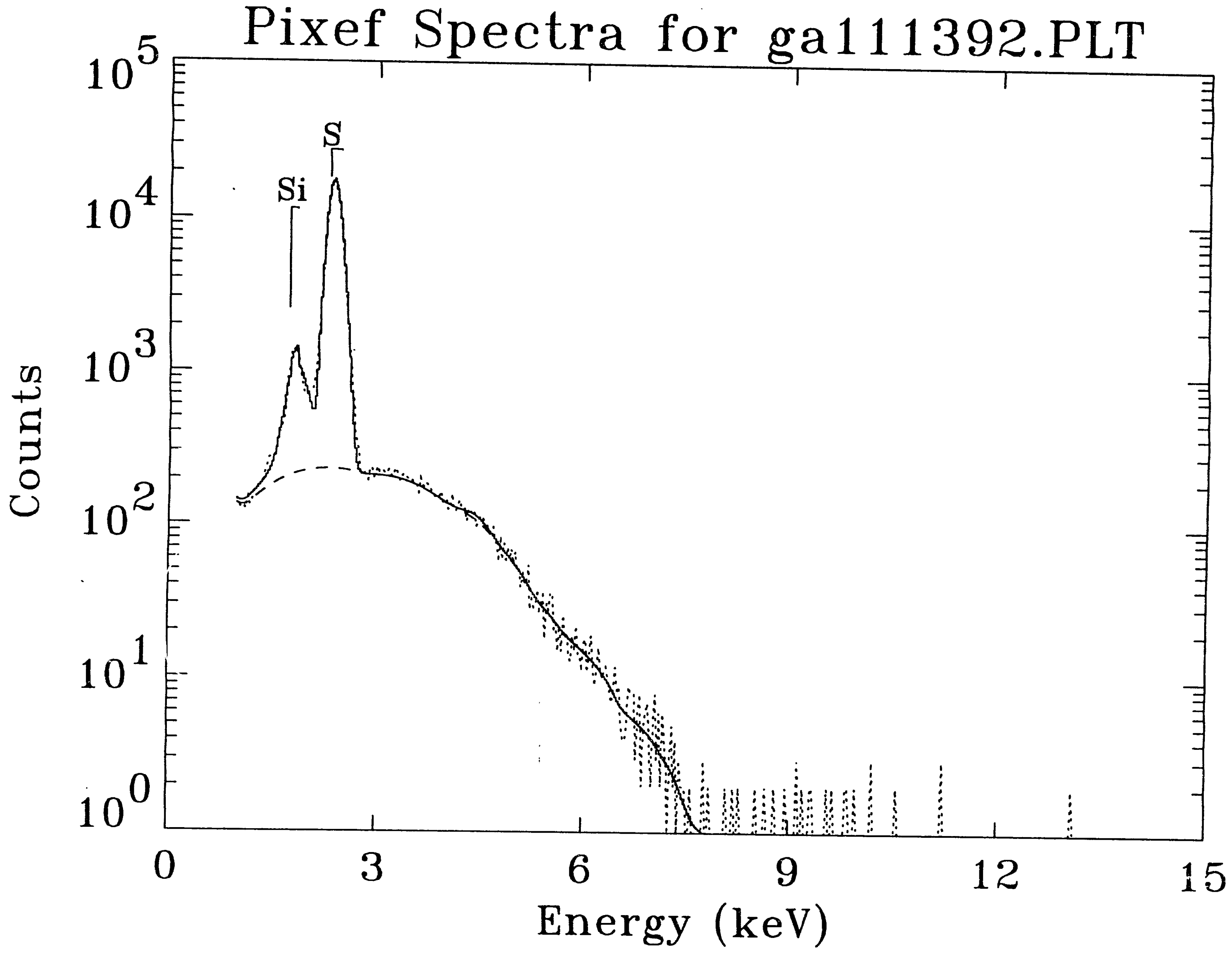


Figure 4.

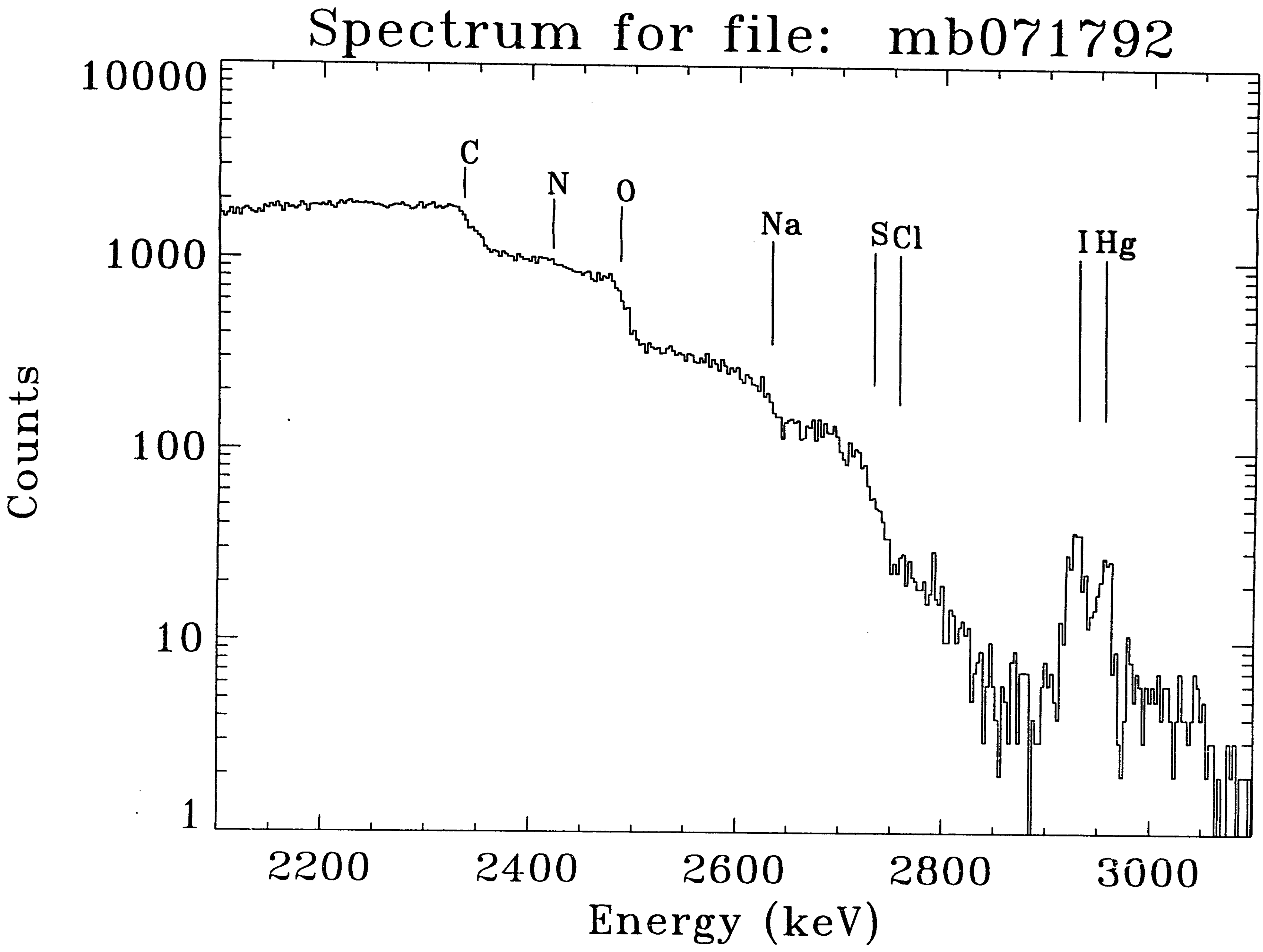
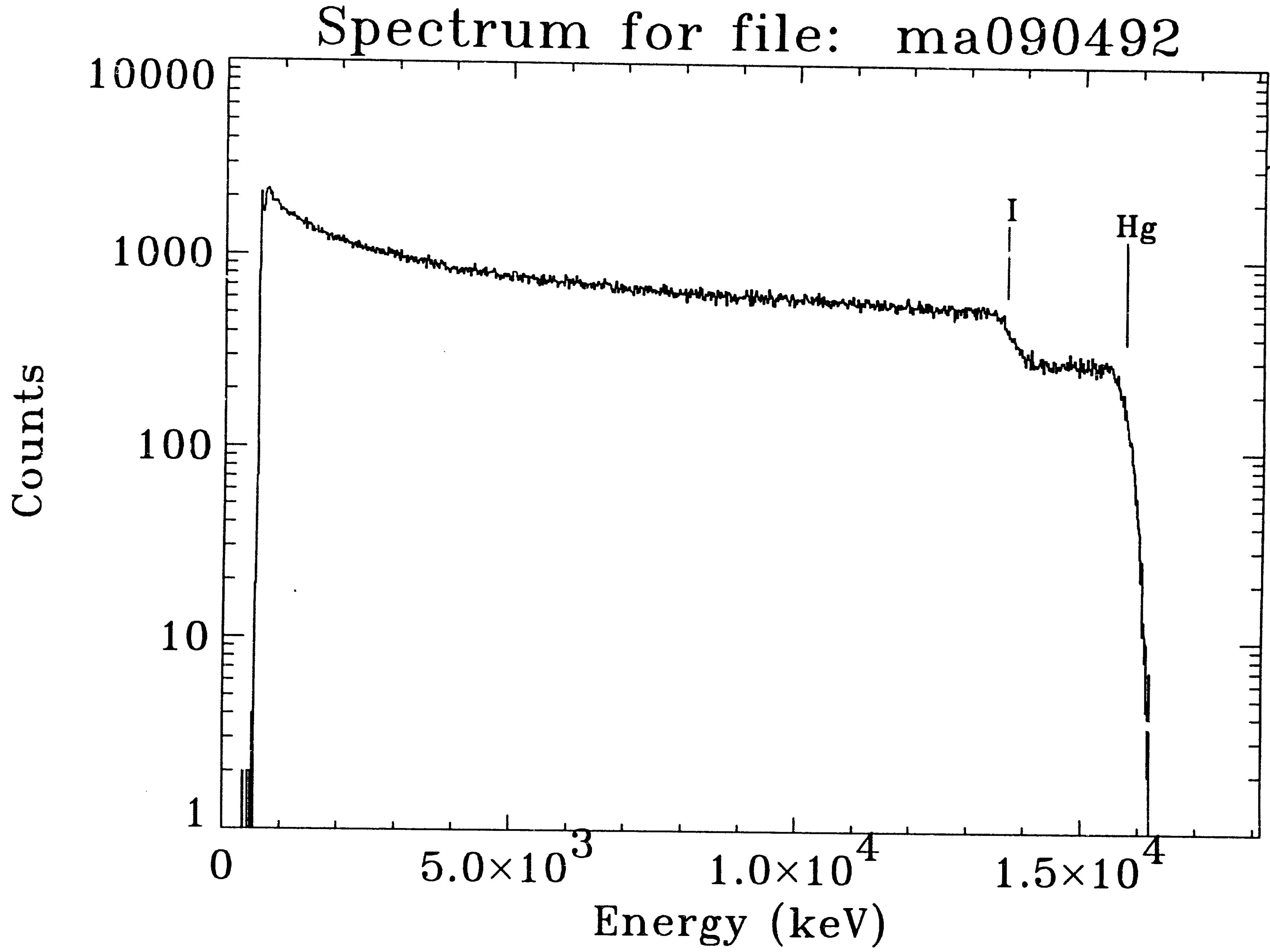


Figure 5.



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