

Broadband, ultrahigh resolution PIXE spectroscopy using TES microcalorimeter arrays

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INTRODUCTION

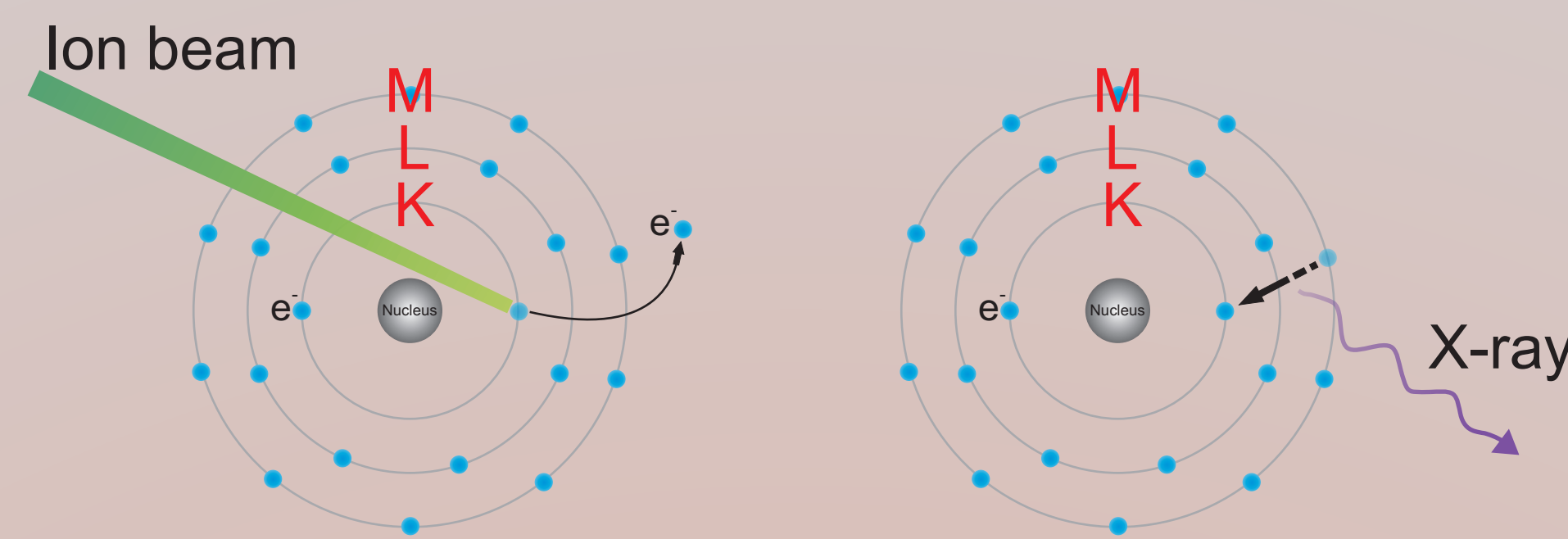
Traditionally, silicon and germanium semiconductor detectors have been employed for particle induced X-ray emission (PIXE), because of their wide energy range, the ease of use and the reasonable cost.

These properties have so far compensated their limited energy resolution (100-150 eV for Mn K α). The wavelength dispersive detectors (WDS), with superb energy resolution (~ 5 eV), have been successfully used for PIXE, but their intrinsically low throughput makes the measurements cumbersome and time consuming.

In a microcalorimeter, such as a superconductive transition-edge sensor (TES), operating at cryogenic temperature, one combines the high efficiency and the wide energy range of energy dispersive detectors, while maintaining the energy resolution similar to the WDS.

PIXE

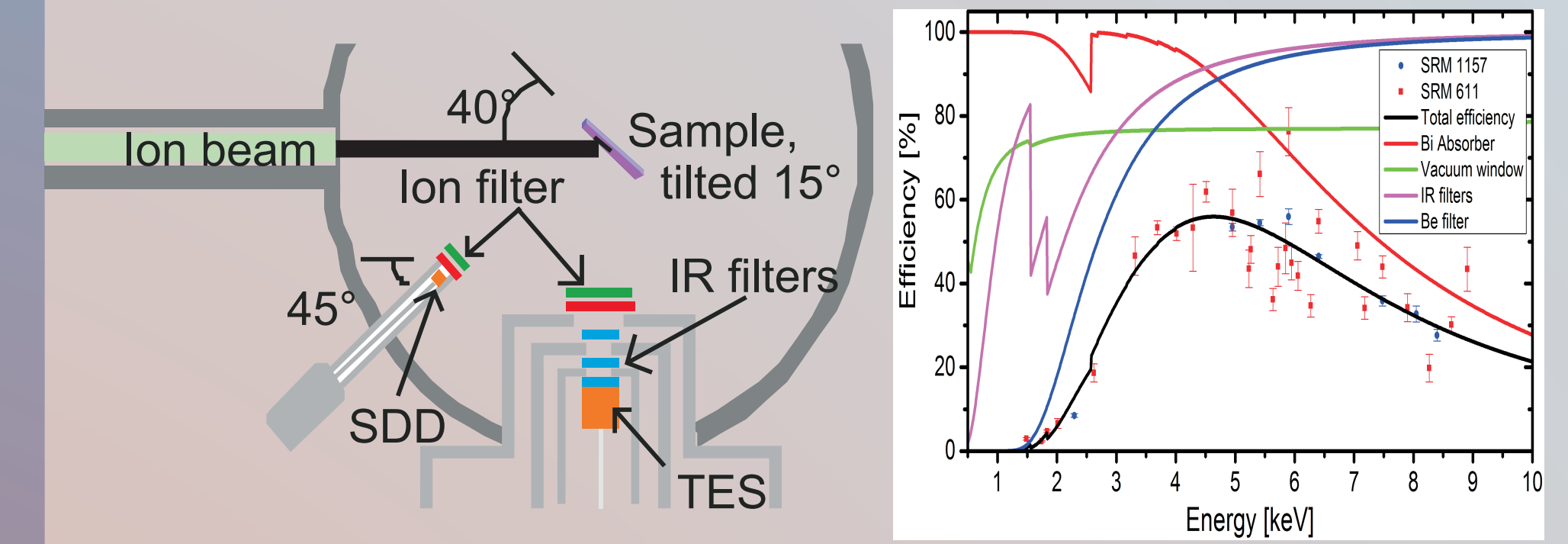
Particle Induced X-ray Emission (PIXE) is a method for determining the elemental composition of a sample by exposing it to an ion beam and measuring the emitted characteristic X-rays.



- Trace element studies even below ppm levels.
- Highest sensitivity with 2-3 MeV protons and for elements with atomic number between 20-40 and over 75.
- Ion beam can be brought to ambient conditions.
- Applications in materials science, medical diagnostics, geology, archeology, art authentication, environmental monitoring.

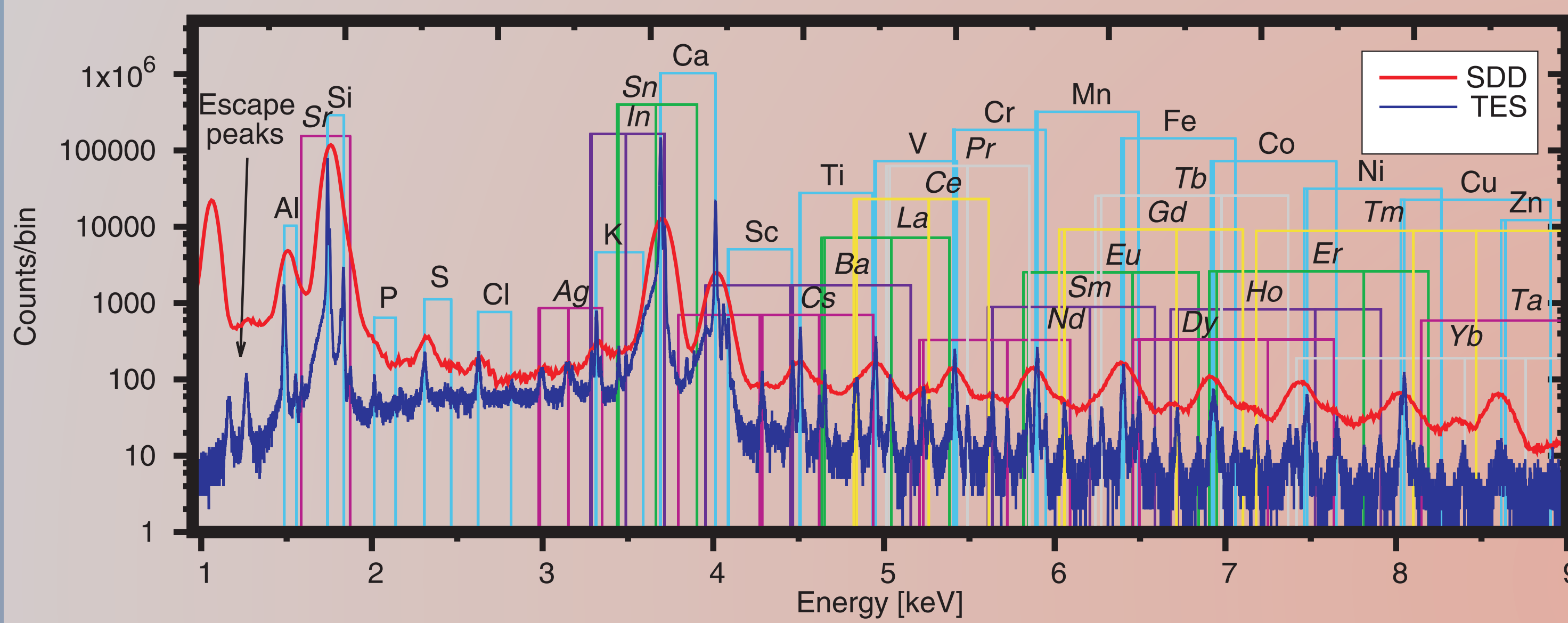
MEASUREMENT SETUP [1]

1.7 MV Pelletron accelerator. Energy range from <200 keV for H, He and O, to close to 15 MeV for multiply charged heavy ions.



- 160 pixel Mo/Cu TES array with Bi absorber (NIST).
- Snout with X-ray window in dry ADR (HPD), NIST SQUID readout with TDM multiplexing.
- 3 eV energy resolution at 5.9 keV (best pixel), ~ 6 eV average for 100 pixel array
- Optimized for 1-10 keV X-rays.

DIFFICULT SAMPLE WITH 61 TRACE IMPURITY ELEMENTS [2]



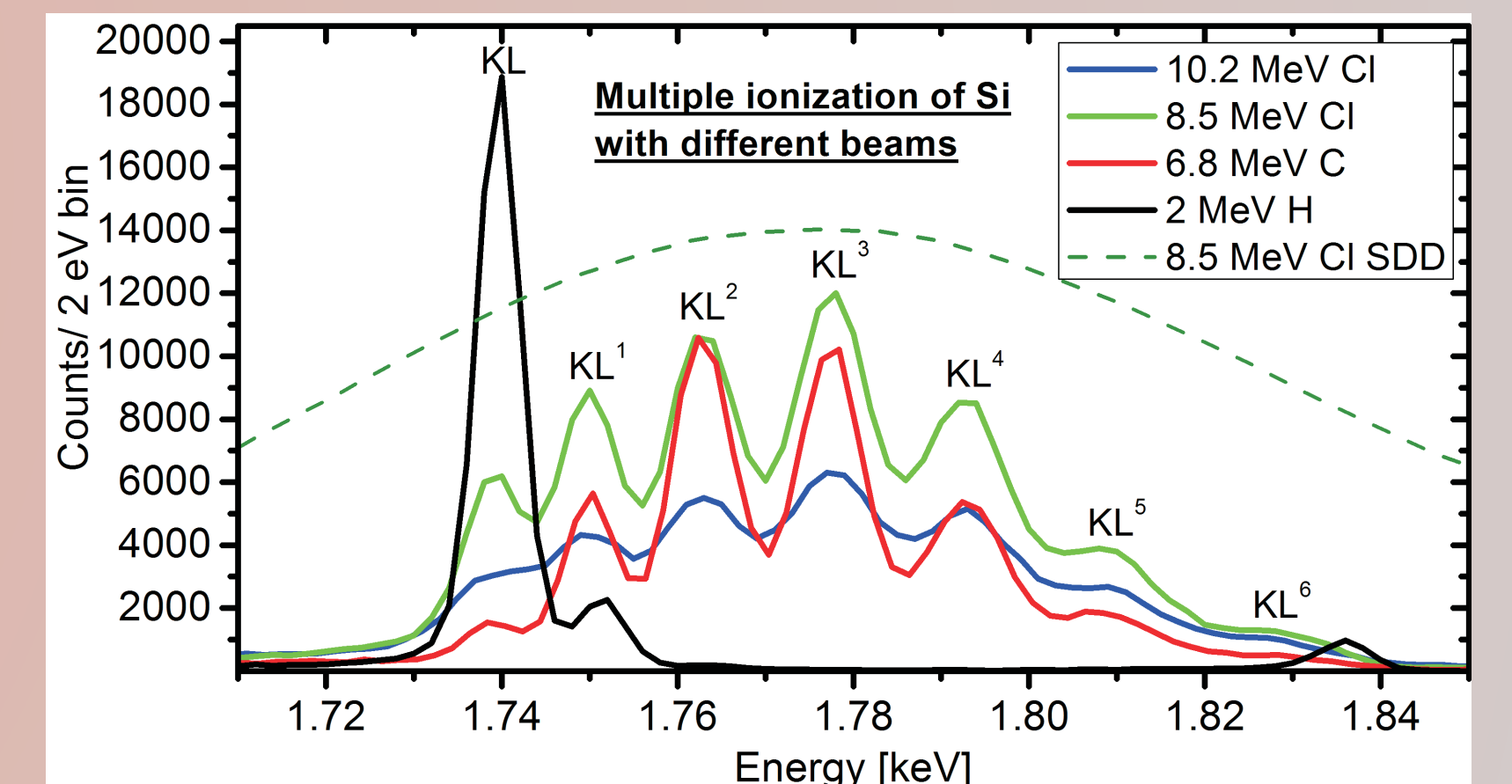
Proton PIXE of NIST reference sample SRM-611 (impurities in glass) demonstrates the superiority of TES over SDD.

All trace elements (100-500 ppm) within the energy range shown identified with TES array.

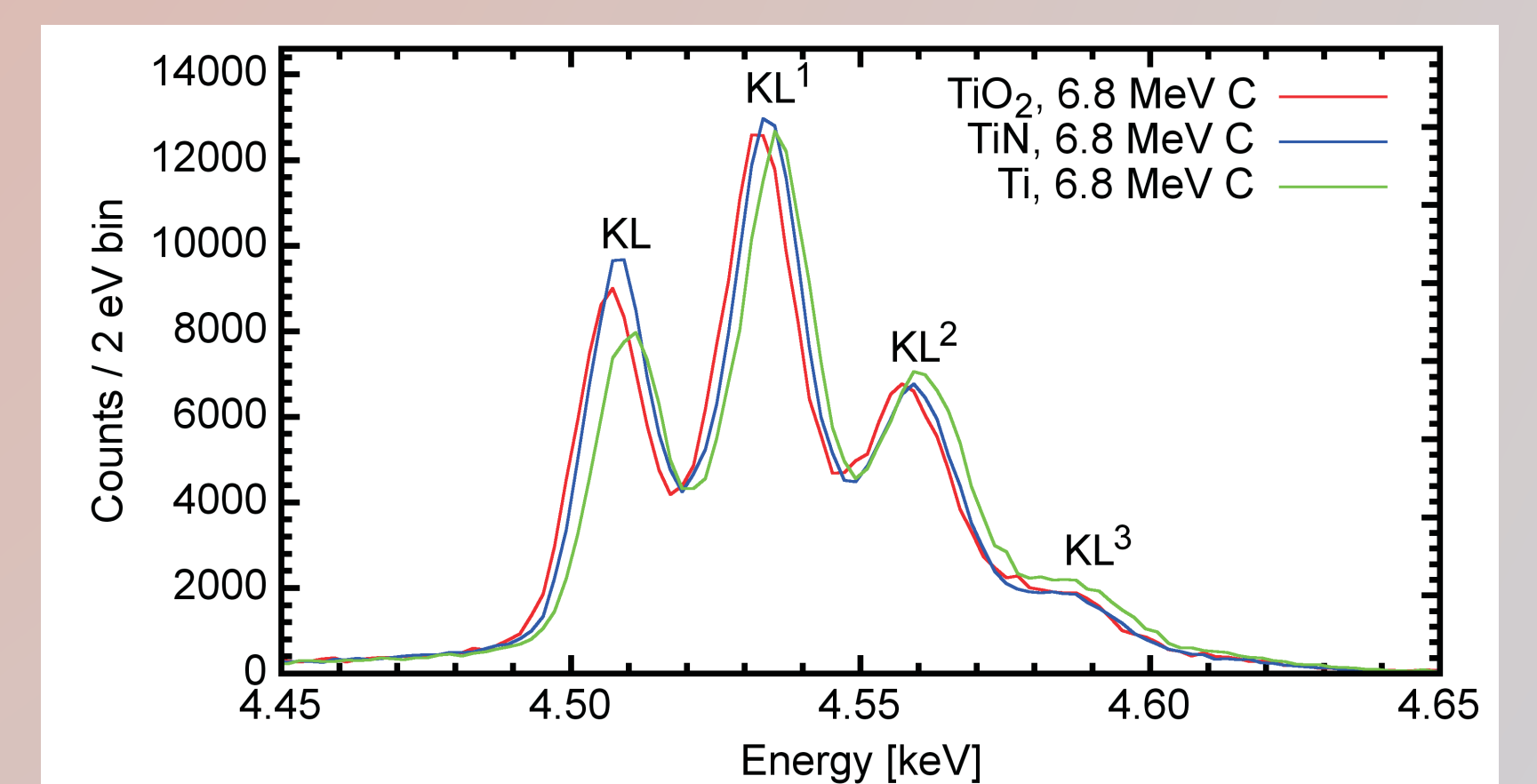
With the used measurement time (4 h) and pixel count (60), detection limits around 10-50 ppm.

HEAVY IONS IN PIXE

- + Higher ionization cross-section.
- + Increases multiple ionization (chemical information).
- + Simultaneous other heavy-ion beam techniques (ToF-ERDA, SIMS).
- ± Less penetrative.
- ± Sensitivity more element specific.
- Increased background.
- More destructive to the sample.
- Requires vacuum.
- Projectile X-rays may be visible.

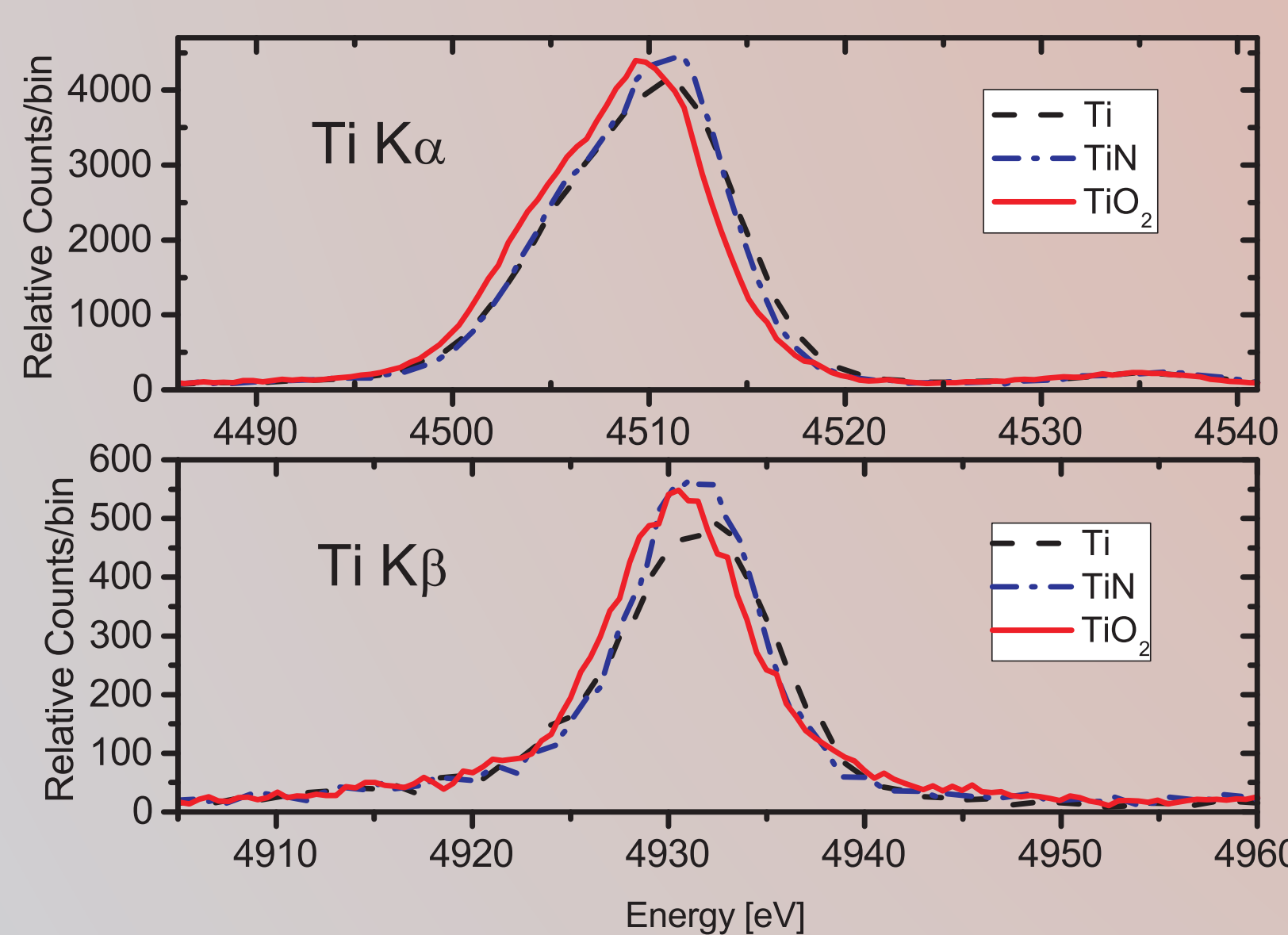


With heavier ions (C and Cl) more multiple ionization than with H. High energy resolution allows the separation of satellite peaks unlike with the SDD.



• Clear differences in KL peak relative intensities for the different compounds (TiO₂, TiN, Ti thin films).

CHEMICAL INFORMATION (SHIFTS, INTENSITIES), PROTON BEAM [2]



The chemical state of an element (oxidation number, chemical bonding) influences its electronic transitions and atomic energy levels, even those of the inner shells of the atoms.

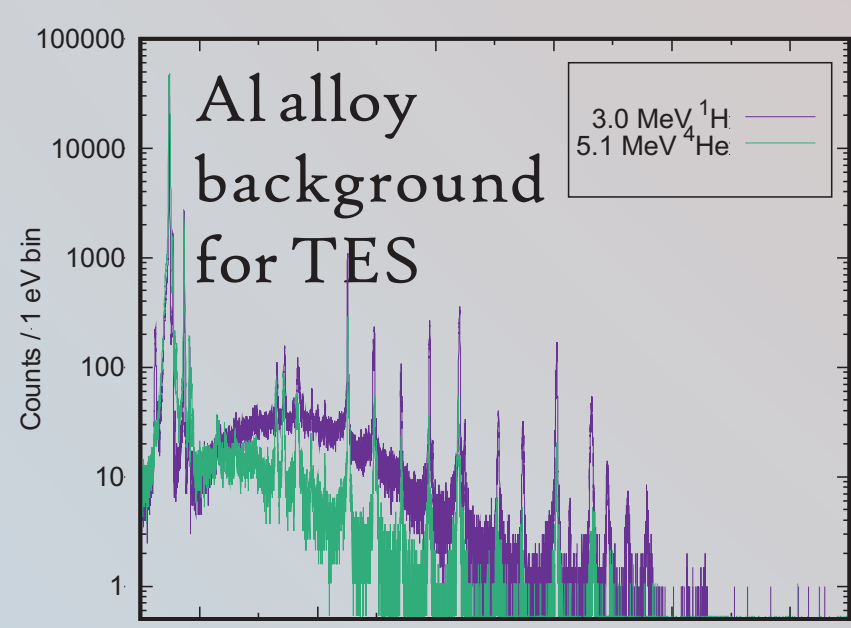
Ti, TiN and TiO₂ thin films were measured to see if the effect of the chemical bond could be seen in the characteristic X-rays of the samples. A 2 MeV proton beam was used to excite the samples.

A chemical shift of (1.1 ± 0.3) eV was measured on the K α complex of the TiO₂ sample compared to the Ti sample and a (1.0 ± 0.3) eV shift was seen in the K β .

In addition, K β /K α intensity ratio was seen to depend on the compound, with values (12.5 \pm 0.1)% for Ti, (13.1 \pm 0.2)% for TiN, and (13.3 \pm 0.2)% for TiO₂.

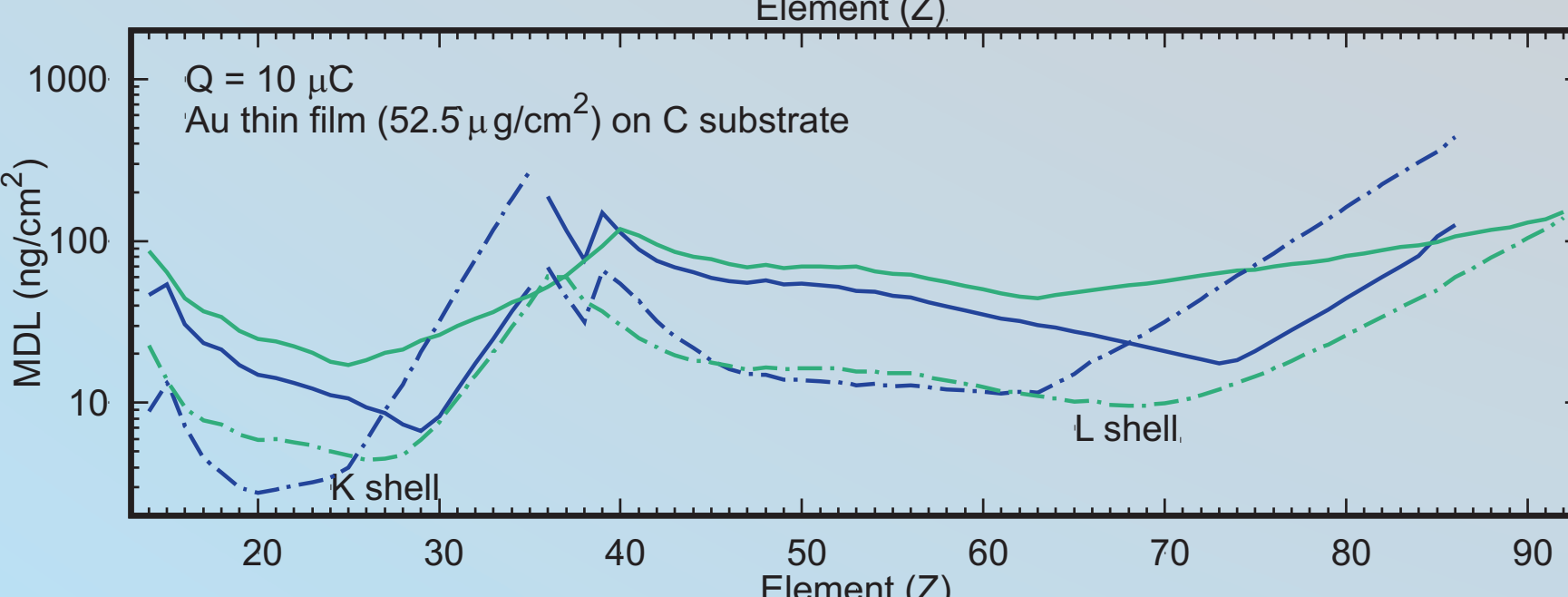
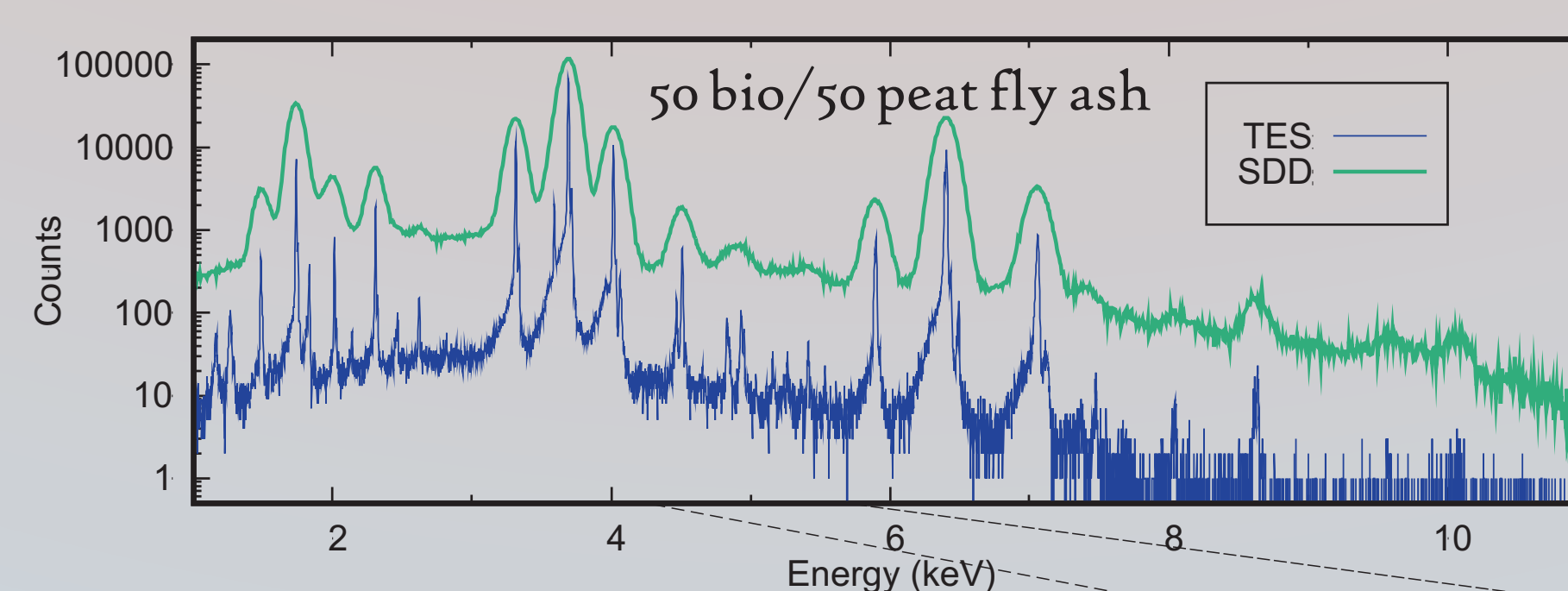
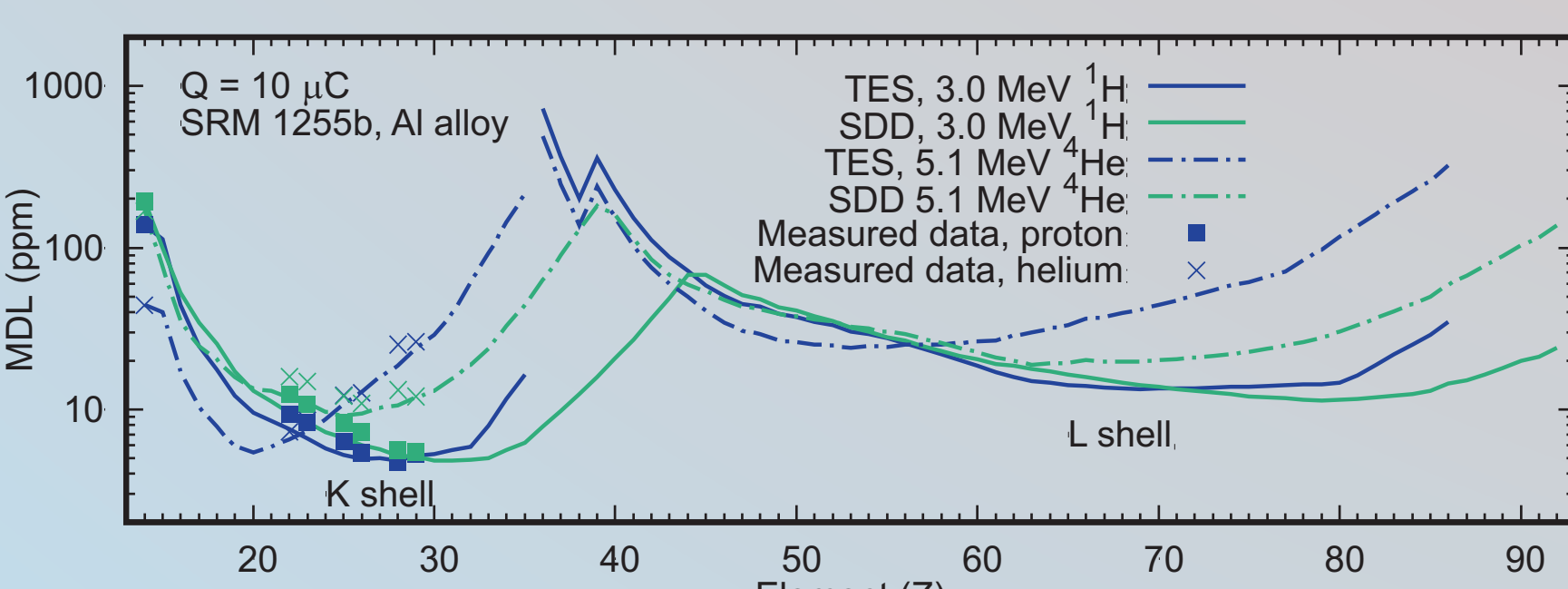
Intensity ratios are a useful option, as they are not sensitive to energy calibration errors, and all compounds gave different values.

DETECTION LIMITS TES VS SDD, H AND HE IRRADIATION [3]

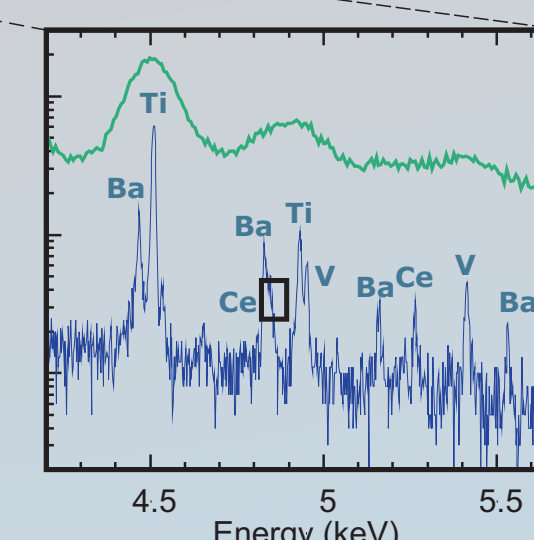


- Minimum detection limits calculated for isolated peaks using measured background, TES with 100 pixels (1-2 h time).
- Element is detected when FWHM area is over 3 times the square root of background, MDL = $3 \sqrt{\text{BG}} / (Y_{\text{th}} \gamma)$, where Y_{th} is the theoretical yield (cross-sections), γ the experimental (setup efficiency)

- For bulk Al alloy, smaller detection limits with proton beam than with He beam, and vice versa for thin film samples.
- SDD is better when the efficiency of the TES detector array starts to drop and the background level becomes so small that higher resolution doesn't give a significant advantage.
- With He beam, the lower background means that SDD has better detection limits than TES for more elements than with H beam.



- Overlapping peaks of Ti (3700 ppm), Ba (4200 ppm), Ce (1300 ppm), and V (200 ppm) are challenging for the SDD, but are nicely separated using TES-array.
- Detection limits are estimated to improve by factors 400-700 by TES (normalized to the same solid angle and efficiency).



CONCLUSIONS

A TES detector array is a powerful tool in PIXE thanks to its great energy resolution and wide energy range, with chemical sensitivity capabilities.

Heavy ion irradiation offers advantages in some cases, multiple ionization satellite peaks give an additional handle on chemistry.

We demonstrated detection limits in the 1-10 ppm range, however, the improvements over SDD are modest in the case of isolated peaks. With overlapping peaks for SDD, TES can give orders of magnitude advantage in detection limits as well as in reliability, due to the separation of the peaks.

REFERENCES

- [1] M. R. J. Palosaari *et al.*, J. Low Temp. Phys. 176, 285-290 (2014)
- [2] M. R. J. Palosaari *et al.*, Phys. Rev. Applied 6, 024002 (2016)
- [3] M. Käyhkö *et al.*, Nucl. Instrum. Methods Phys. Res. B, in press (2017), available online.