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PIGE analysis of Fluorine in materials for the circular economy

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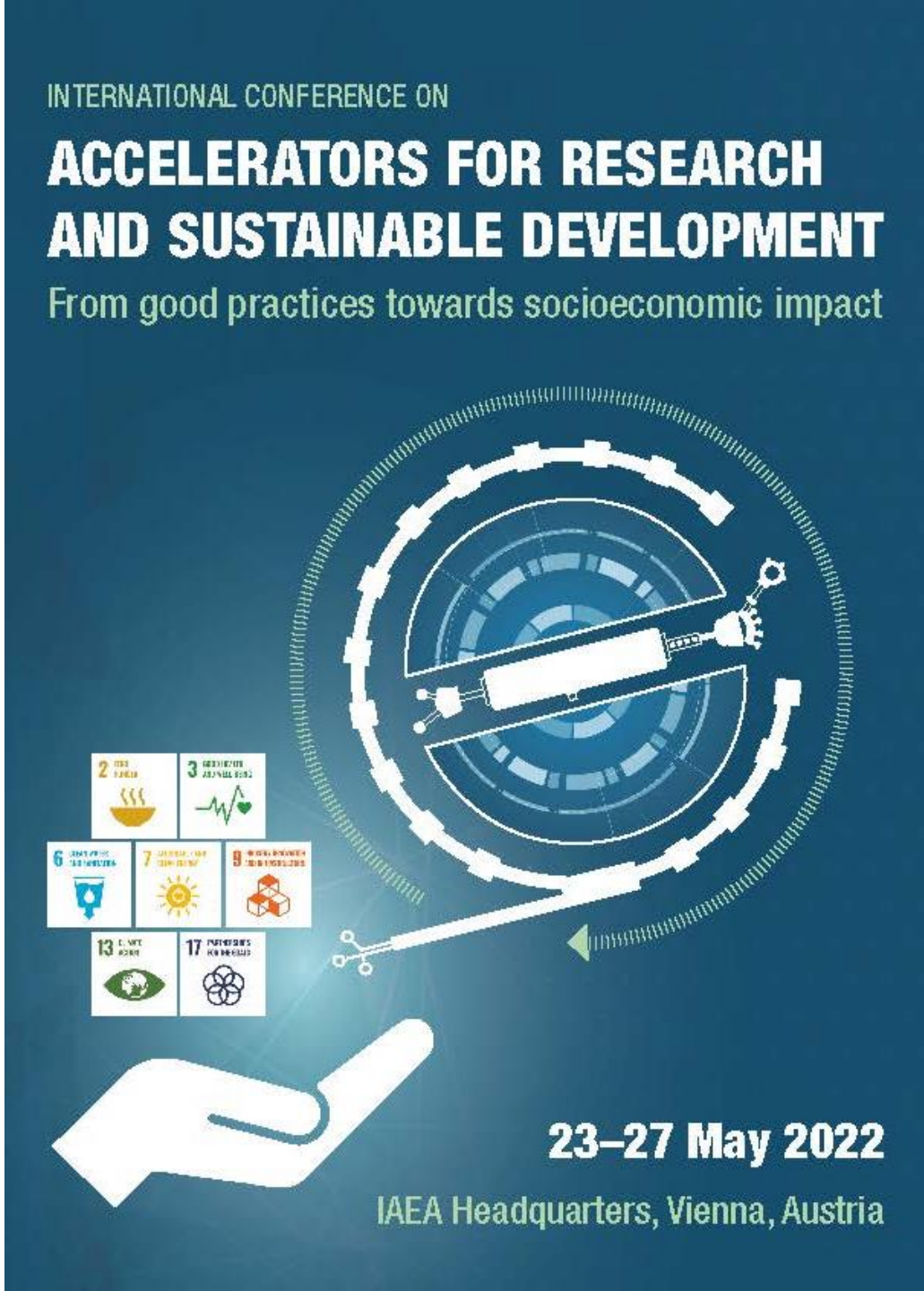


Introduction

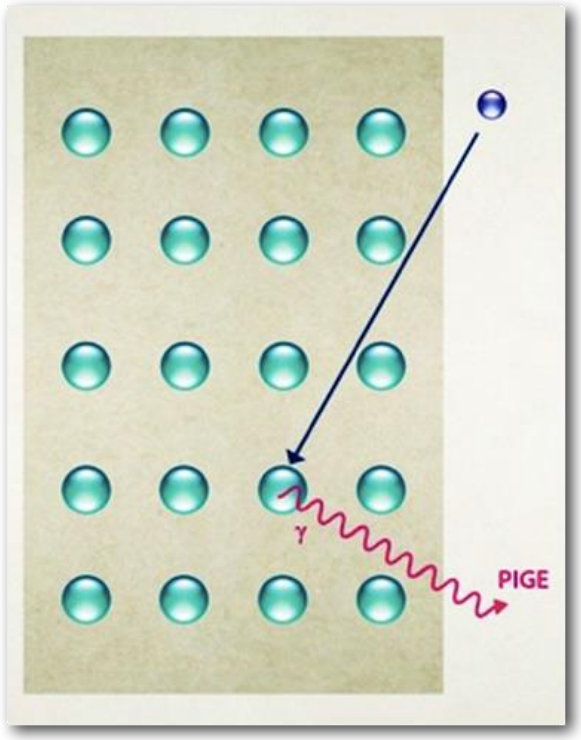
- Per- and polyfluoroalkyl substances (PFASs) are highly persistent synthetic chemicals, some of which have been associated with cancer, developmental toxicity, immunotoxicity, and other health effects
- PFASs are widely used in non-stick, stain-resistant, and waterproof consumer products, such as food and beverage containers, because of their hydrophobic and lipophobic properties

Introduction

- PFASs in grease-resistant recyclable food packaging can leach into food and increase dietary exposure, and can also contribute to environmental contamination during production and disposal
- PFASs are typically detected and quantified by liquid chromatography mass spectrometry (LC-MS) if an adequate standard exists

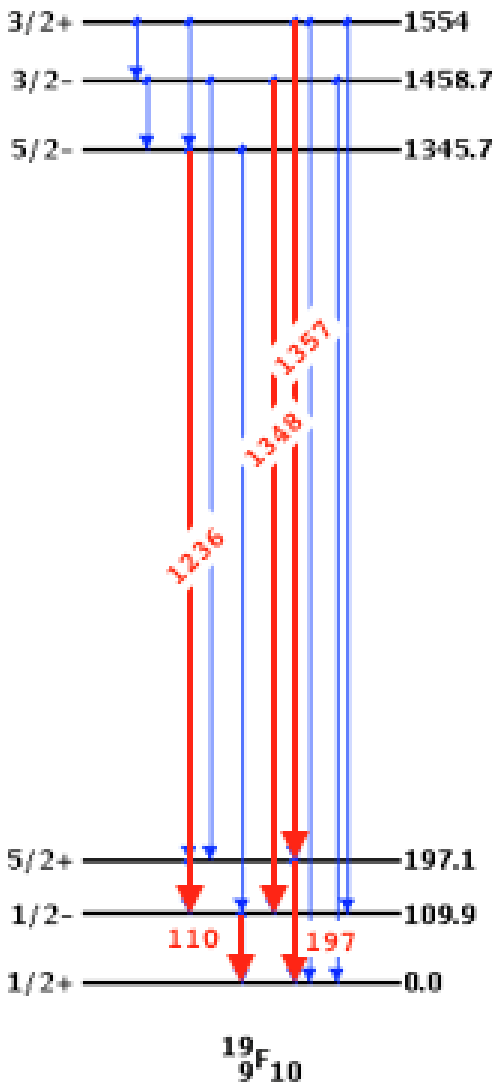
Methodology

- Particle induced gamma-ray emission (PIGE) technique is based on detection of characteristic gamma-rays promptly emitted during the ion beam irradiation
- PIGE is mostly used when the chemical composition of the sample is qualitatively known, and a particular gamma-reaction is used to quantify the concentration of a specific isotope



Methodology

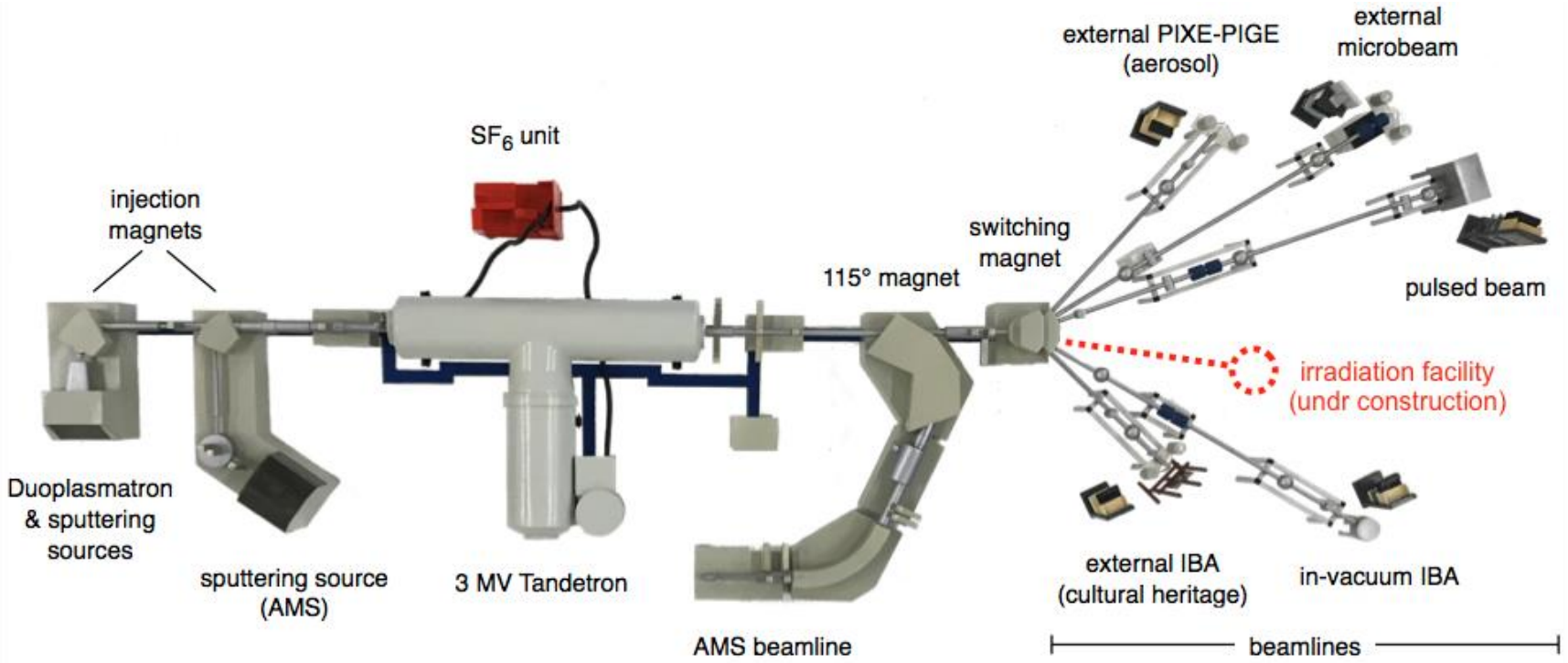
- The total fluorine content in a sample can be determined by detecting several characteristic gamma-rays, in particular those at 197 keV emitted from the de-excitation of ^{19}F in the $^{19}F(p,p'\gamma_{2-0})^{19}F$ inelastic reaction
- A standard-less PIGE analysis can be implemented to determine F in a solid sample



Samples

- 36 samples of food paperboard containers (plates, bowls) and beverage containers (cups) from cafeterias, canteens and supermarkets were collected in different Italian cities

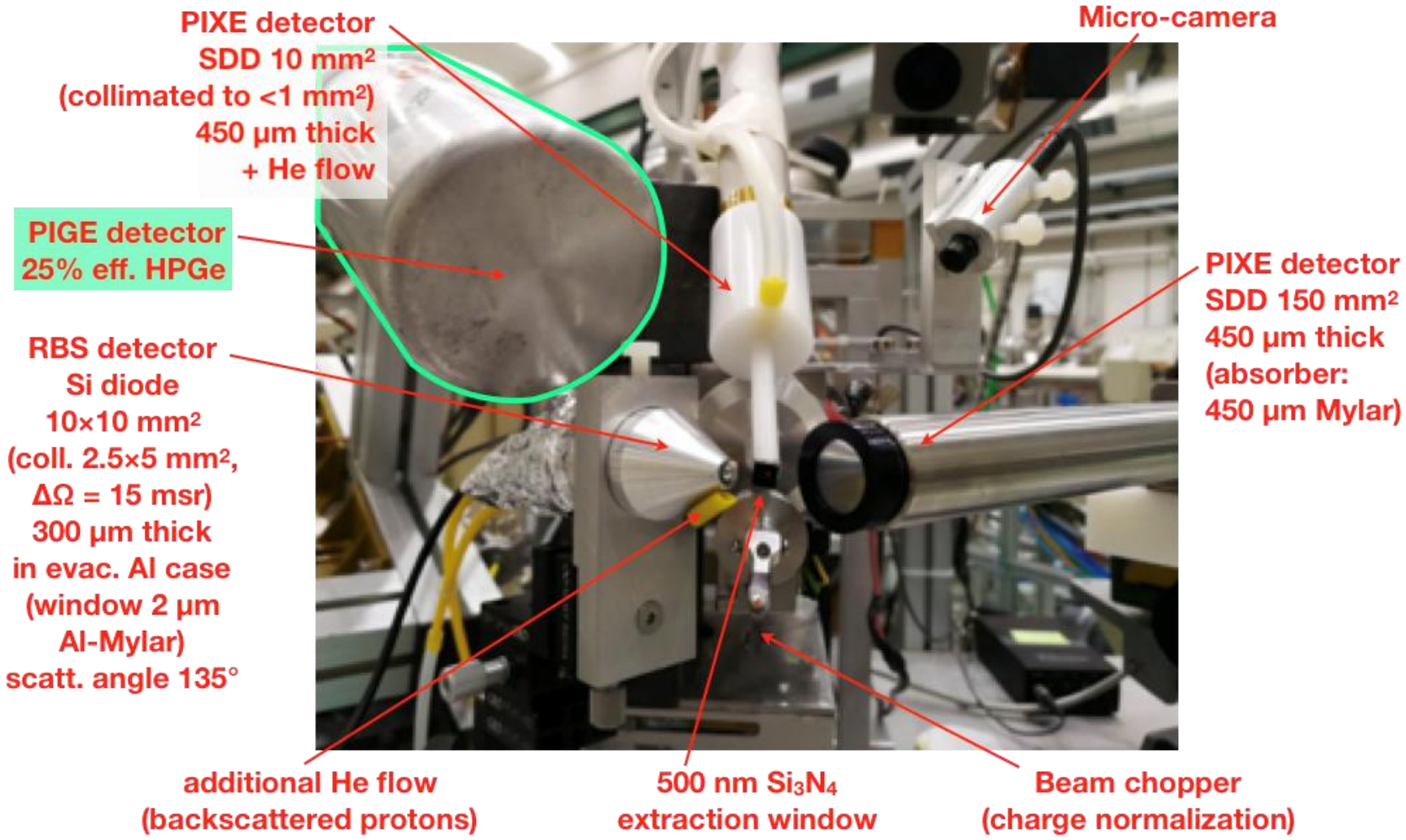
LABEC, Laboratory of Nuclear Techniques for the Environment and Cutural Heritage, Florence, Italy



- 3 MV HVEE Tandetron accelerator
- 3 independent ion sources
- 5 beamlines for IBA (3 external-beamlines)
- 1 beamline for AMS

- XRF laboratories (Epsilon 5, custom portable XRF scanners)
- AMS sample prep labs

External beam set-up (cultural heritage)

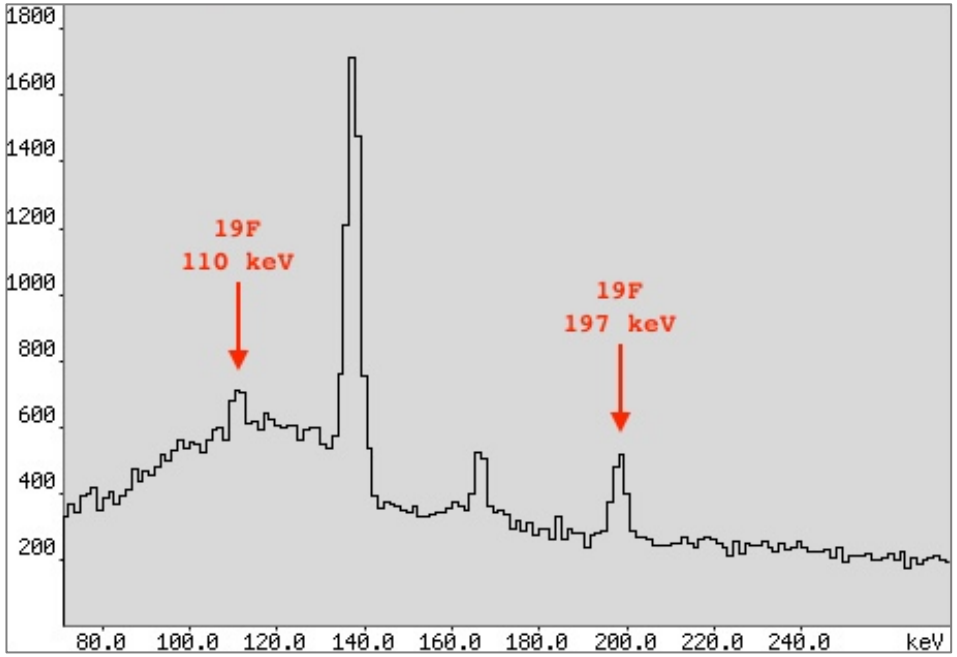


Experimental parameters

- 4 MeV proton beam
- External beam measurements (the samples are analysed “as is”)
- 100-250 pA beam current
- 300-400 s measurement time
- 1 cm^2 analysed area (by continuously scanning the sample; the beam spot size is < 1 mm)
- HPGe placed at 135°

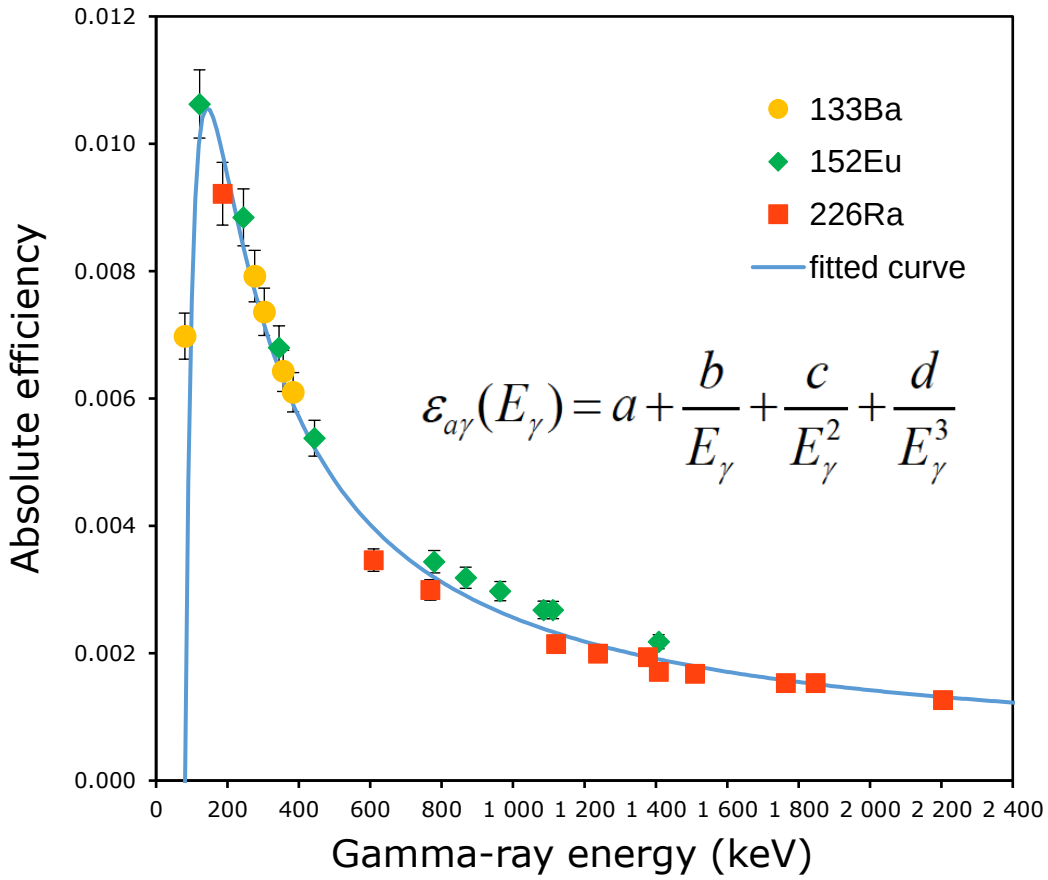
Data analysis

- The yield of the 197 keV from the $^{19}F(p,p'\gamma_{2-0})^{19}F$ reaction was used to determine F concentration in bulk samples
- Standard-less analysis of PIGE measurements with the PIGRECO code (http://tandem.inp.demokritos.gr/pigreco) using experimental parameters (i.e. absolute dectect efficiency), ZBL stopping power and measured differential cross sections of $p+^{19}F$ reaction



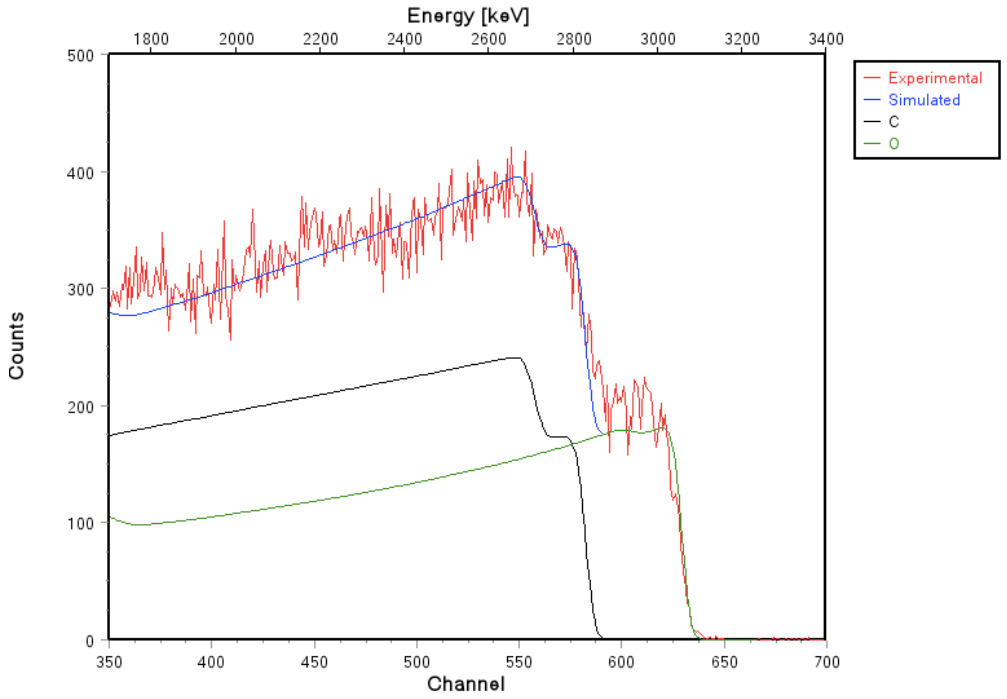
Detector efficiency

- The measurement of the absolute efficiency of the HPGe detector was carried out using calibrated radioactive sources (^{133}Ba, ^{152}Eu and ^{226}Ra) placed at the exact position of the target
- The efficiency at 197 keV was obtained by fitting the experimental data with a polynomial curve in the argument of $1/E_\gamma$



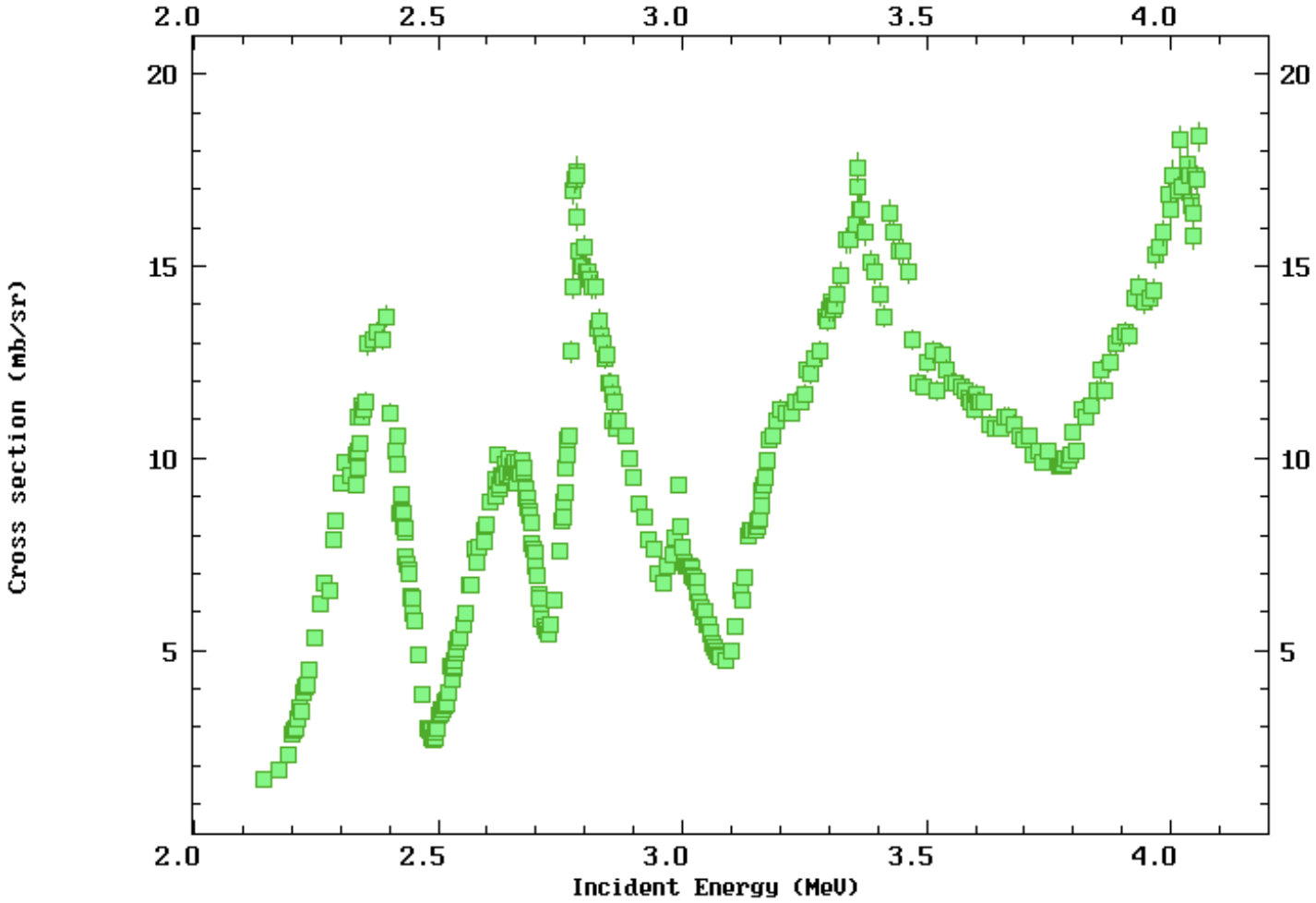
Sample bulk composition

- Simultaneous EBS measurements allowed to determine the samples bulk matrix for stopping power calculation, such as 14% H, 57% C and 29% O for lot 1 samples
- H is an «invisible» element whose concentration is a free parameter of the fit of the simulated to the experimental spectrum
- PIXE measurements revealed the presence of Mg, Si, S, Cl, K, Ca, Fe and Zr as minor or trace elements



Gamma-ray differential cross-section

- The data from Jesus et al. IAEA-TECDOC-1822, Vienna (2017), were used as differential cross section for the reaction
- These data are available from the IAEA IBANDL data library



Uncertainty budget

Source	Value	Type
Counting statistics/peak fitting	8%-20%	Statistical
Beam charge measurement	1%	Statistical
Background subtraction	15%	Systematic
Detector absolute efficiency	7%	Systematic
Gamma-ray emission cross section [1]	7%	Systematic
Stopping power [2]	4%	Systematic
Total statistial contribution	8%-12%	Statistical
Total systematic contribution	18%	Systematic
Total uncertainty	20%-27%	Statistical+Systematic

[1] A.P. Jesus et al., IAEA-TECDOC-1822, Vienna (2017)
[2] J.F. Ziegler et al., "SRIM – The stopping and range of ions in matter (2010)", Nucl. Instr. Meth. B 268 (2010) 1818

Results

Source	Sample type	# samples	F concentraion (ppm)
Supermarket in Rome	Plate	15	990 ± 200
Cafeteria in Bologna	Bowl Cup	1 4	830 ± 200 470 ± 120
Cafeteria in Rome (1)	Plate	1	1130 ± 240
Cafeteria in Rome (2)	Plate Lid	1 1	840 ± 190 <LOD
Cafeteria in Milan	Plate Bowl Cup Food container w/lid	3 3 4 1	850 ± 210 620 ± 165 <LOD 550 ± 140
Cafeteria in Rome (3)	Bowl	1	410 ± 110
Cafeteria in Ferrara	Plate	1	2030 ± 710

LOD were in the 200-300 ppm range, varying mainly with the beam intensity

Conclusions

- This study demonstrated how standard-less external-beam PIGE can be very useful for rapidly measuring total fluorine in as-is solid samples, without any pre-treatment
- The discovery of fluorinated chemicals in food and beverage containers demonstrates their potentially significant contribution to dietary PFAS exposure and environmental contamination during production and disposal
- The methodology has been applied also to determine total fluorine in luxury textiles (work in progress)

Remarks

- Transnational access to LABEC for similar studies will be possible starting from September 2022 thanks to the Horizon Europe 101058414 project Remade@ARI (Recyclable Materials Development at Analytical Research Infrastructures)
- Now Transnational access to LABEC is possible through the EU H2020 RADIATE project (G.A. 824096), please visit the website: https://www.ionbeamcenters.eu/radiate/radiate-transnational-access/

Thank you

Acknowledgements

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