Mass spectrometry: critical aspects related to the particles detection in the Condensed Matter Nuclear Science

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SUMMARY

- **Mass spectrometry**
  - *potentiality of the technique*
  - *details on the measurement*

- **Critical aspects and experimental requirements for:**
  - *mass spectrometer*
  - *measurement apparatus*

- **Experimental set up at ENEA and some results**

Mass spectrometry

Potentiality of the technique

- ☐ *To detect ^4He during electrochemical loading of palladium lattice with deuterium assuming that the heat excess comes from the nuclear reaction:*

  $D+D = {}^4He$ + heat (24 MeV for event)

  giving ^4He + energy as final products

- ☐ *To reveal possible deviation of isotopic composition on metallic thin films electrochemically loaded of hydrogen. This result should be the evidence of nuclear processes.*

Details on the measurement

Mass spectrometry allows to identify:

a. *Molecular weight of elements/compounds*

b. *Molecular weight of relative "fragments"*

c. *The chemical formula of the compound (for high mass resolution analyzers with $m/\Delta m > 500$)*

example	Low Resolution	High Resolution
Species (?)	44	44.06276
CS	44	43.97207
CO_2	44	43.98980
C_3H_8	44	44.06264

To detect ^{4}He:

mass spectrometer operates in RGA (Residual Gas Analyser) configuration

The sample is the neutral gas coming from the electrolytic cell.

The gas is ionized and then analysed inside the spectrometer

To measure the isotopic composition:

mass spectrometer operates in SIMS (Secondary Ion Mass Spectrometry) configuration

The sample is the surface of the electrolysed metallic film under a flux of energetic (primary) Ar ions.

The positive and negative (secondary) ions emitted from the surface are directly analysed inside the spectrometer

Critical aspects
and
experimental requirements

Requirements for the mass spectrometer

For ^{4}He measurements (RGA) and for Isotopic ratio measurements (SIMS)

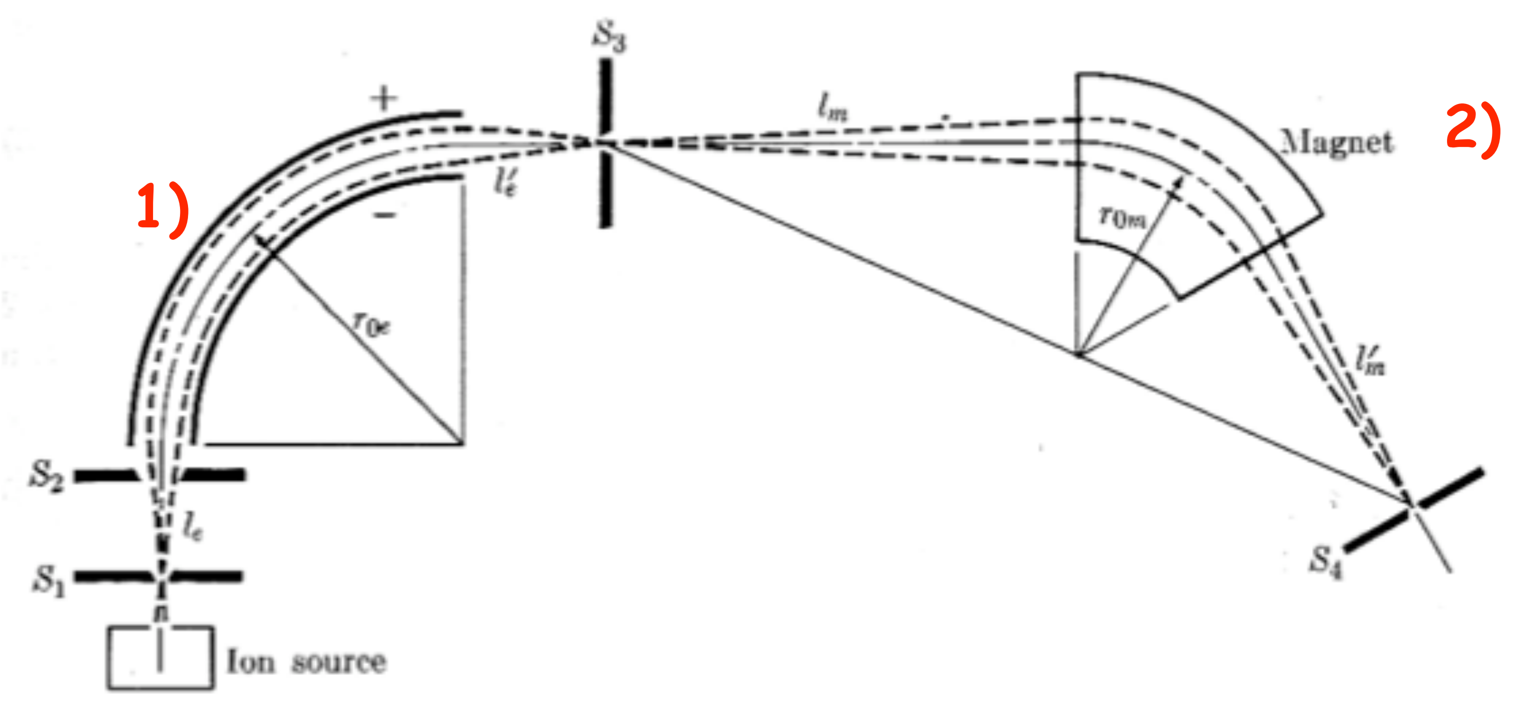
the instrument must have:

- high mass resolution
- high sensitivity
- high stability

☐ Magnetic+electrostatic analyser fulfills all the requirements. The surface contamination inside the system is less likely to result in degraded sensitivity due to the high ions energy. It is a good choice.

☐ Quadrupole mass analyser is less suitable because sensitivity and stability can be strongly reduced by surface contamination

Magnetic + electrostatic mass analyser



Magnetic analyser alone (2) is not enough to have high mass resolution since it selects only momentum. Selection in energy is made with an electrostatic analyser (1)
Double focalization: 1) in energy in S3 by an electrostatic deflector and 2) in momentum in S4 by a magnetic deflector

Requirements for ^{4}He apparatus

It is crucial to minimize ^{4}He background and to have a good reproducibility of the measurement.

Therefore:

a. Avoid air leaks, minimize He permeation from the external atmosphere (5.2 ppm of He in air)

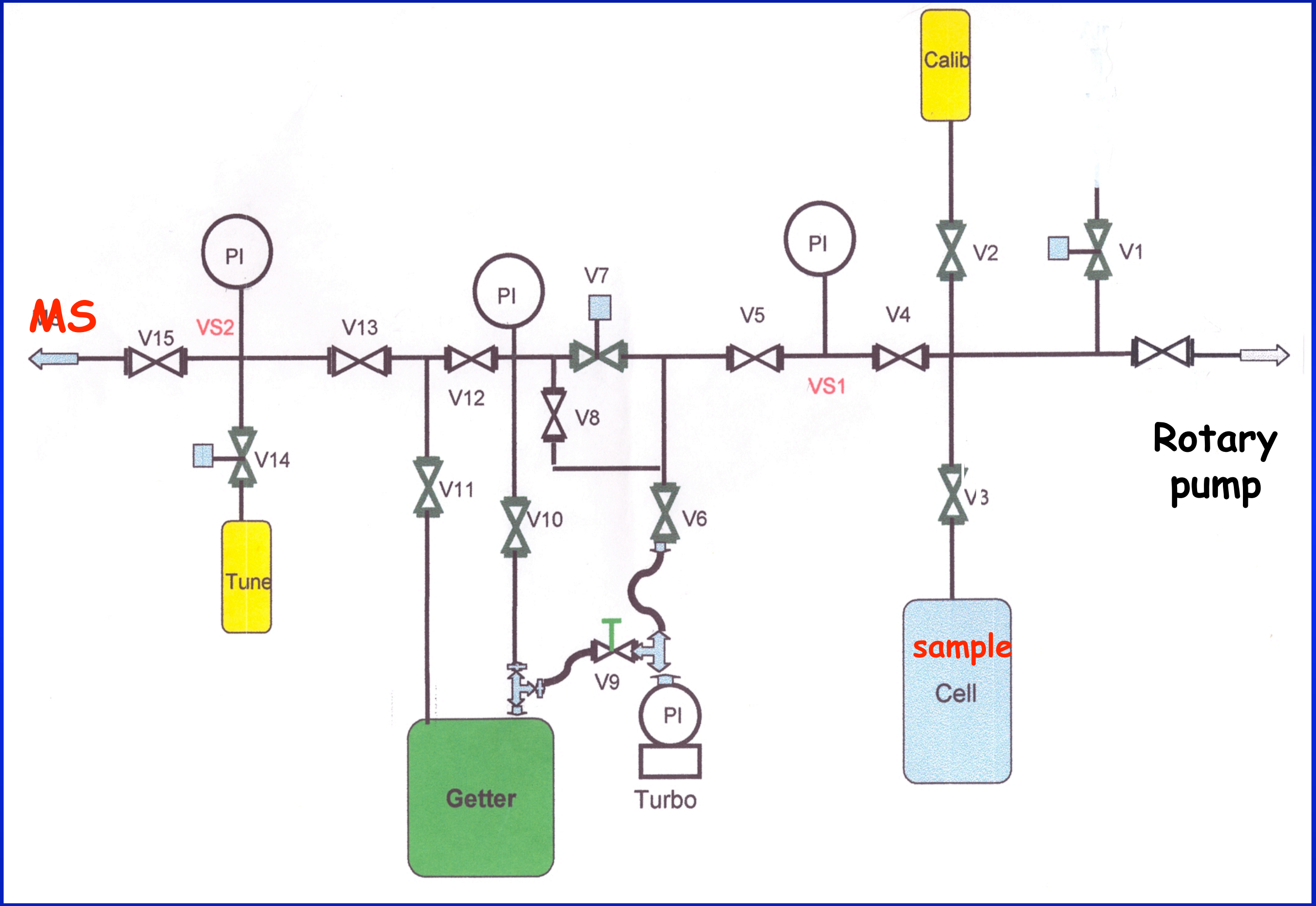
b. Reduce spurious gases by thermal desorption. Purge the gas sample by means a selective pump that absorbs active gases but not He (es: getter pumps)

c. Calibrate the mass spectrometer to quantify the measurement

d. Measure the He background and its reproducibility

Experimental set up in the Condensed Matter Nuclear Science laboratory at ENEA and some results

^{4}He apparatus



The Mass Spectrometer (MS) is a high resolution and high sensitivity Jeol CG-Mate magnetic + electrostatic mass analyser

Preliminary measurements can be found in (*)

(*) ICCF11:*Review of recent work at ENEA*

Secondary Ion Mass Spectrometry (SIMS)

- Very suitable technique to reveal small traces of surface elements or compounds (not quantitative)
- Very accurate measurements of isotopic ratio
- Dynamic SIMS allows depth profile of elements/compounds concentration

The SIMS available in ENEA-Frascati is:

Leybold SSM200-Mass Spectrometer Module

(Leybold IQE 12/38 ion source and Balzers Quadrupole Mass Analyser with ion optics)

- **Primary beam:**

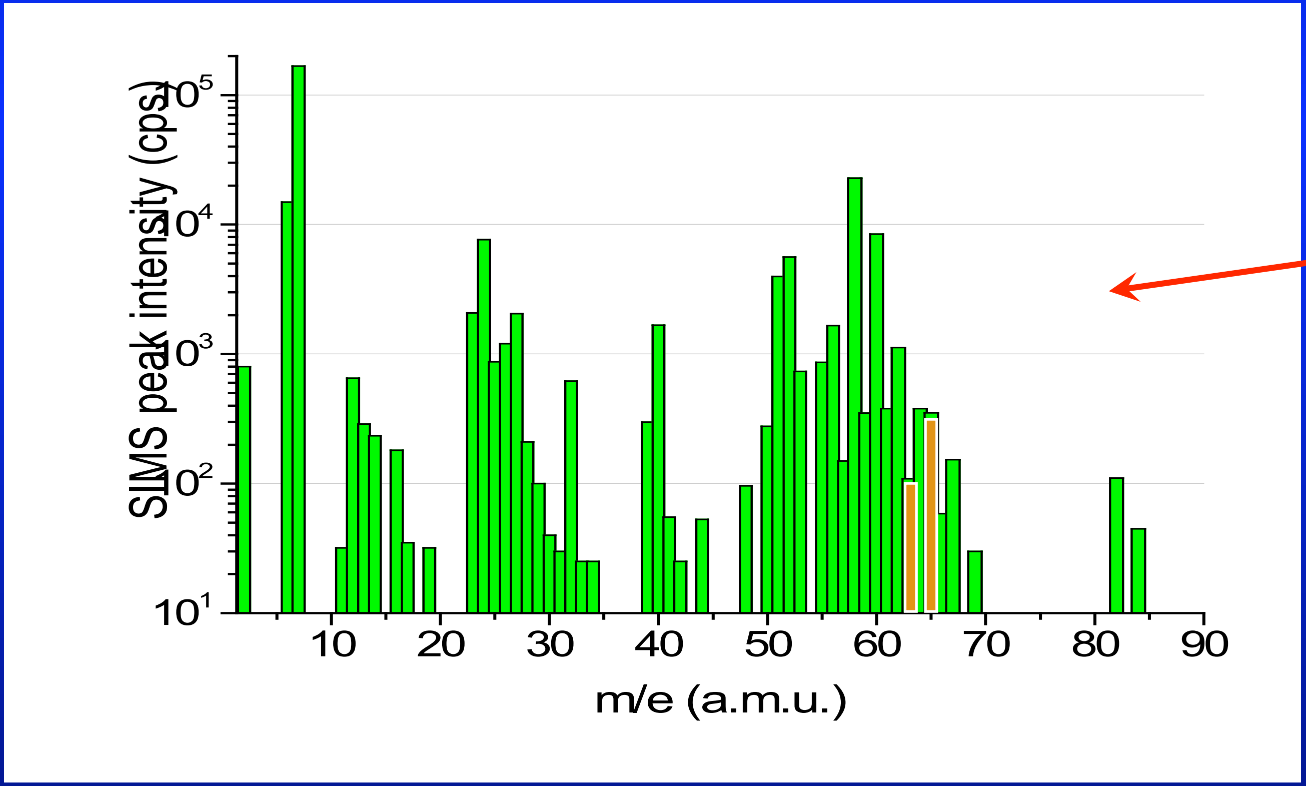
  heavy ions [Ar^+], spot ∅≈2mm, I≈0.5-2 μA, E=1-5 KeV, 45°
- **Emergent particles:** Positive and negative ions
- **Mass range:** m/q≥1 [0-511 a.m.u.]
- **Resolution:** 0.5 a.m.u.
- **Sensitivity:** 10^{12} at/cm^2 (0.1% of 1 atomic monolayer)

Previous Results

SIMS analysis on Ni thin films indicated an apparent isotopic shift on the 63/65 Cu masses ***(Cu has these only two isotopes!)***

$^{63}Cu/^{65}Cu \cong 0.12$ (in electrolyzed film)

$^{63}Cu/^{65}Cu \cong 3.3$ (in the reference film) close to 2.25 (natural ratio)



But in the spectrum many other peaks appear that have to be identified

A carefull investigation (*) of the mass spectra on the full mass range was carried out to exclude the contribution of other ionic compounds on 65 m/q signal:

1. Double ionized atoms (with the same m/q value)
2. Organic contaminants (giving 65 mass fragments)
3. $^{58}Ni^{7}Li$ due to Li_2SO_4 electrolyte
4. ^{64}NiH compound

But our SIMS resolution is about 100 ($m/\Delta m$), not enough to resolve different peaks with the same nominal mass.

A suitable and very high performance experimental apparatus is required for this study
(for $\Delta m \leq 0.02$, $m/\Delta m > 3000$)

(*) ICCF11: *Progress on the Study of Isotopic Composition in Metallic Thin Films undergone to Electrochemical Loading of Hydrogen*

For a better understanding

A couple of our reference and active samples have been also analysed by two other facilities:

- ☐ **Super-SIMS facility at PSI-ETH (Zurich)**

The apparatus allows to exclude mass interferences from organic molecules and/or fragments

The results show that:

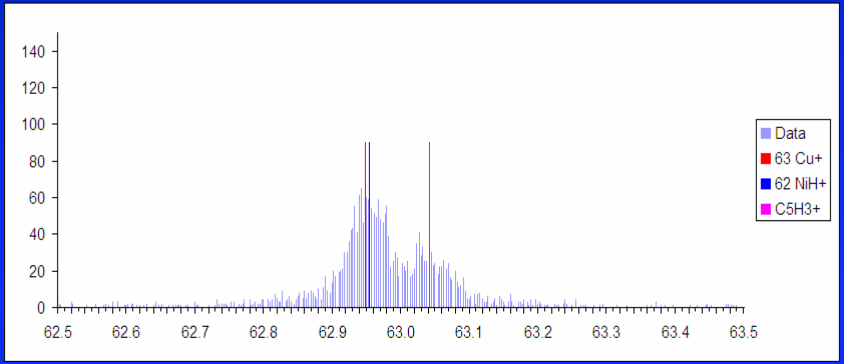
Electrolysed sample: $^{63}Cu/^{65}Cu = 2.40 \pm 0.31$

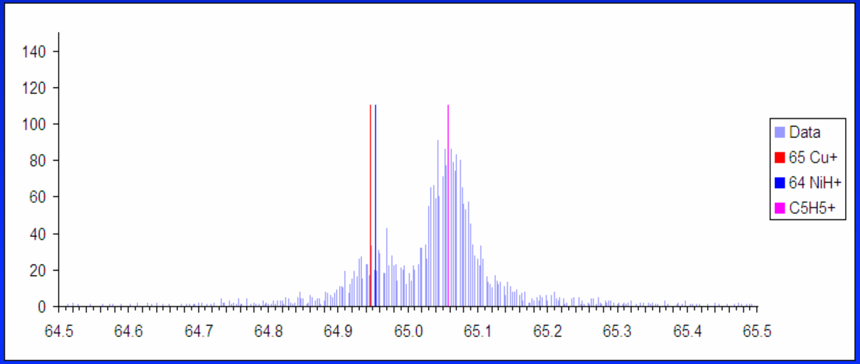
Reference sample: $^{63}Cu/^{65}Cu = 1.79 \pm 0.02$

Cu is present in both active and reference samples, but with a natural isotopic ratio

❑ High resolution time of flight (ToF) MiniSIMS (*Millbrook Instruments UK*)

The apparatus allows to distinguish a single ionized atom from an organic fragment at the same nominal mass.





The results show that:

at the nominal mass of 63 and 65 a.u. the instruments reveals the presence of organic fragments : C_5H_3 and C_5H_5

Copper is detected as a trace contaminant, with a natural isotopic ratio in both samples

CONCLUSIONS

Preliminary results gave evidence of an apparent isotopic shift on the Cu masses (65 too high) in Ni hydrogenated films **but:**

- Cross-matched analysis with two other suitable instruments denied the results, showing that they were an instrumental artefact.

What we learn is that:

- Critical analysis of all the experimental results is mandatory
- The system complexity and the very small size of the foreseen effects require suitable and very high performance experimental apparatus
- Cross-matched analysis are necessary to check preliminary conclusions