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# Study of low- and hyperthermal energy $Ne^+$ scattering from metal surfaces using mass-resolved ion-scattering spectrometry

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# Contents :

- **Mass-resolved Ion Scattering Spectrometry (MARISS):**
  - Basic principles
  - Experimental set-up
- **The study of neutralization of low-energy (0.5-1.5 keV) $Ne^+$ scattered from the Cu-group metals and Pt:**
  - Updated dual-isotope method.
- **Hyperthermal (< 200 eV) $Ne^+$scattering off Au and Pt:**
  - High energy peak (??)
- **Summary**

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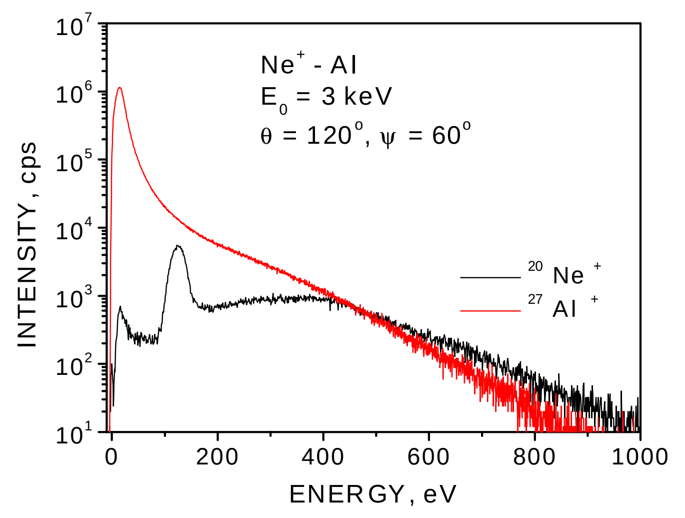
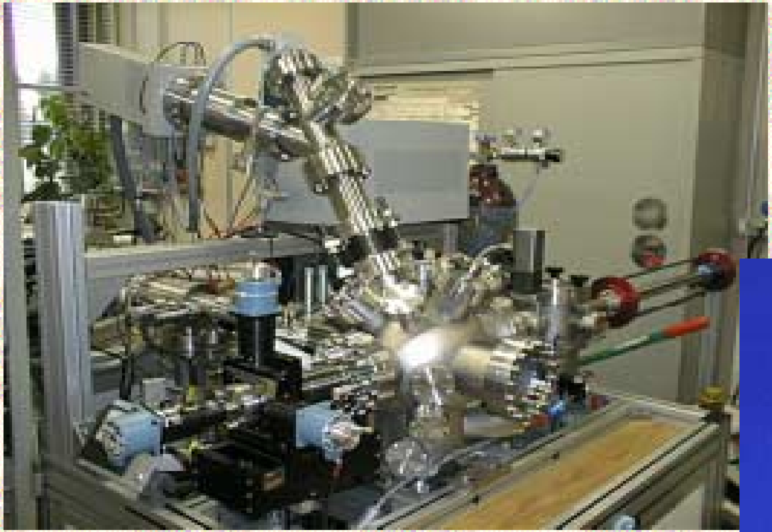
# Compared with conventional low-energy ion scattering (LEIS), the MARISS technique:

- avoids interference between scattered and sputtered ions;
- suppresses the background related to doubly (or multiply) charged ions;
- provides a useful opportunity to operate with a “mixed” primary-ion beam containing different types of projectiles



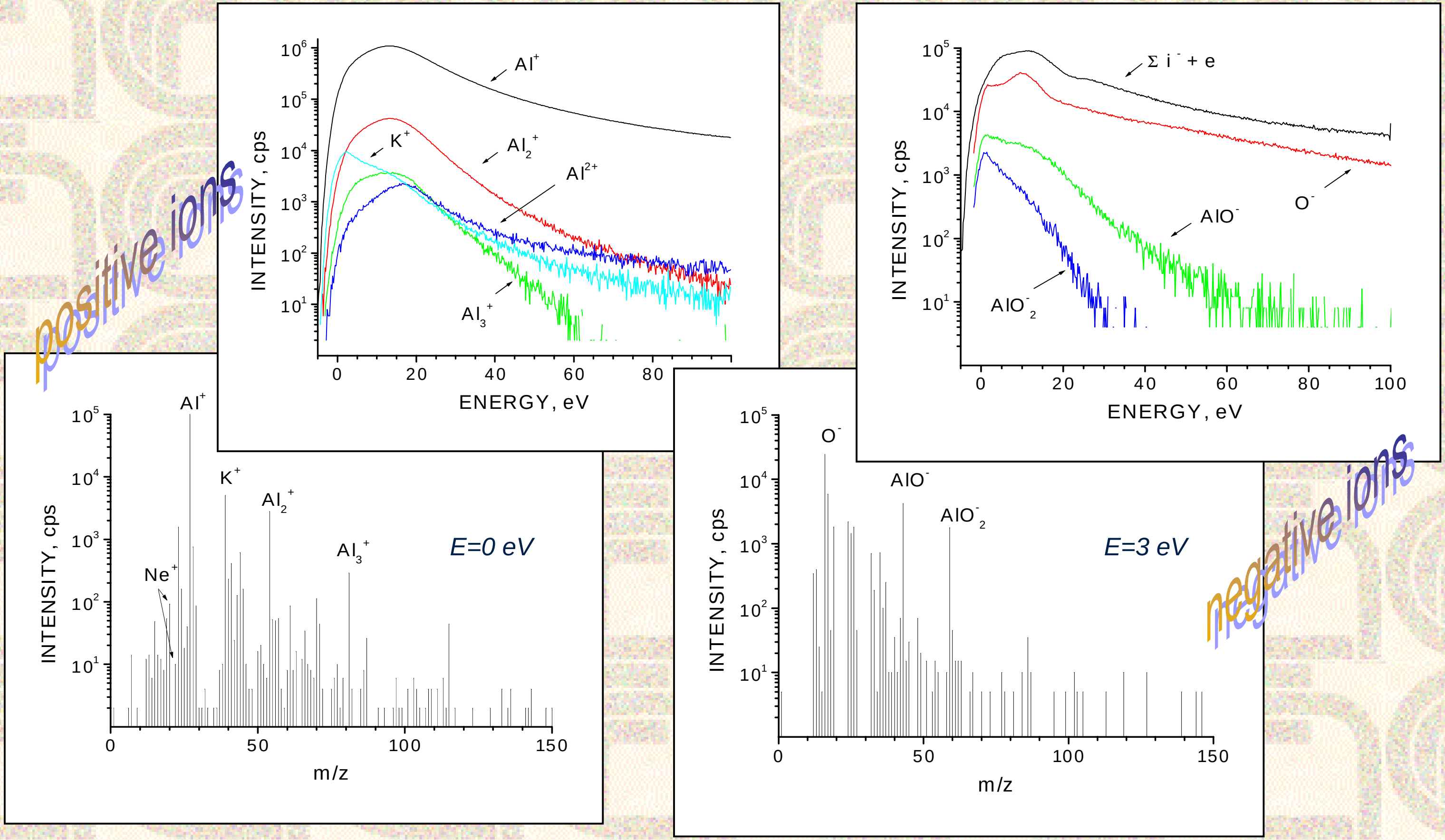
# Custom-built MARISS-SIMS instrument



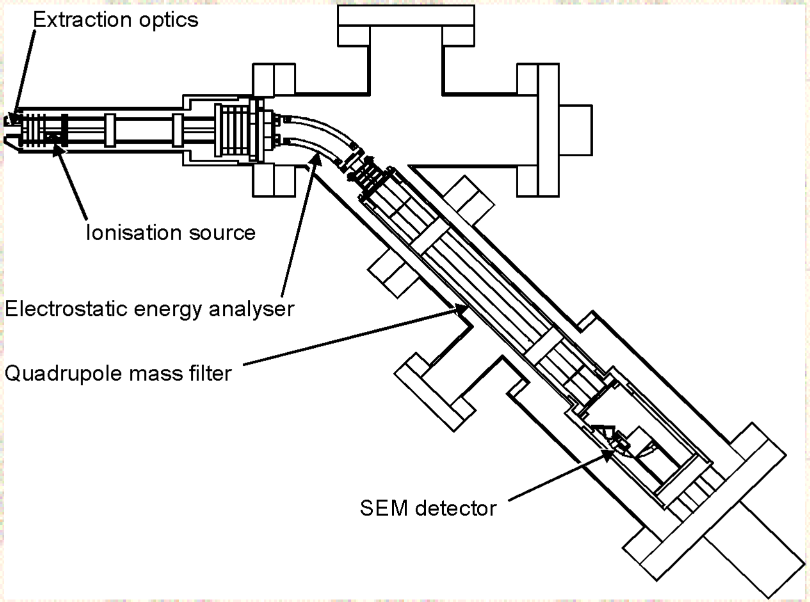
General view

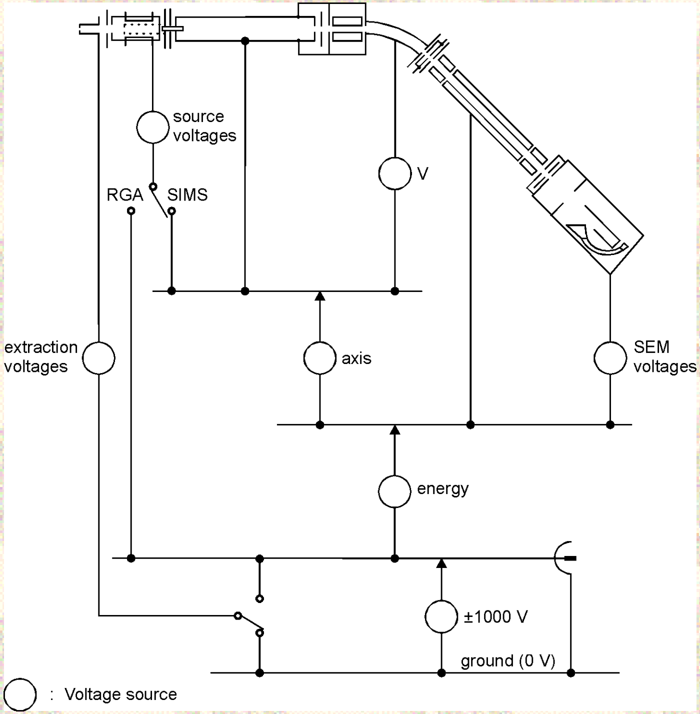
Hiden EQS 1000 Mass Energy Analyser

# Our MARISS-SIMS set-up measures both *energy resolved mass spectra* and *mass resolved energy distributions*



# Hiden EQS 1000 Mass Energy Analyser

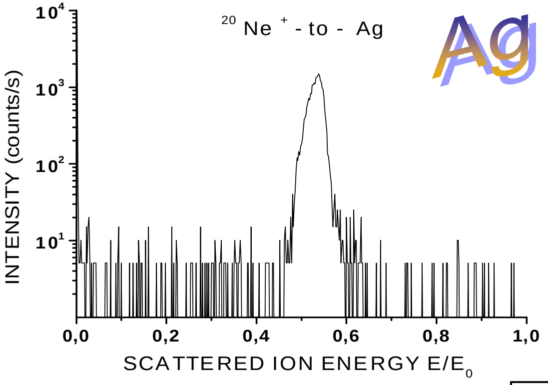


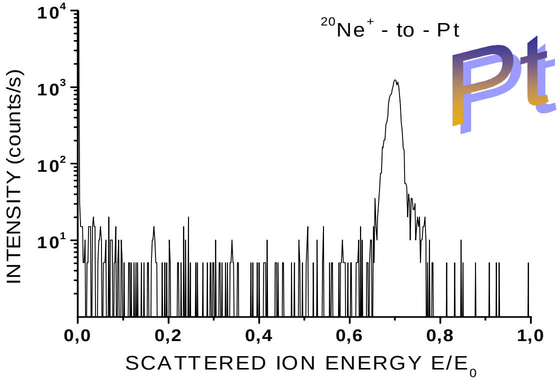


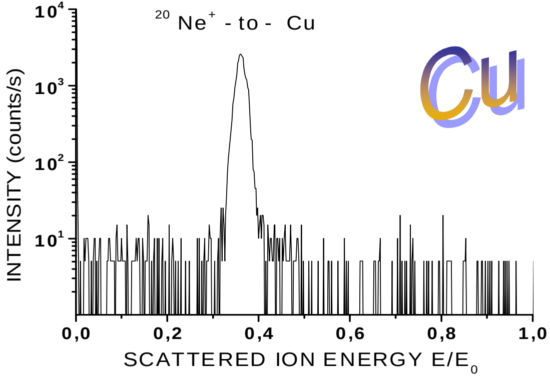
# Experimental Conditions

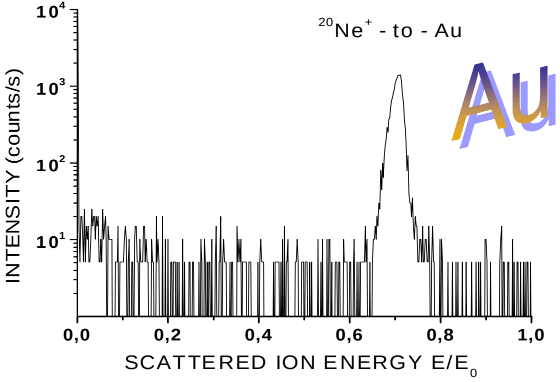
- **EQS 1000 Mass Energy Analyser :**
  - *energy resolution $\Delta E_a$=3.5 eV (FWHM) at $E_a$=80 eV;*
  - *energy scan of ±1100 eV;*
  - *mass resolution $m/\Delta m$ =(5-10)m (FWHM) in the mass range 1-1000 m/z.*
- **3M inert gas ion source:**
  - *energy $E_0$=0.05 -5 keV with $\Delta E_0$=2-4 eV ($I_{em}$=10-15 mA, $U_i$=70-80 V, $p=10^{-5}$ Torr, 99.99% pure Ne, without mass-separation);*
  - *current $I_0$=10 - 1000 nA with $d_0 < 3$ mm and angular divergence $\Delta\gamma$ =0.01-0.05 rad.*
- **“In-plane” specular reflection geometry:**
  - *scattering angle $\theta$=120° with $\Delta\theta$=1° ($\Delta\Omega = 10^{-4}$ sr);*
  - *incident angle $\psi$=60° (on the sample surface).*
- **Samples studied were pure (99.9 %), polished, polycrystalline Cu, Ag, Au and Pt.**

# Mass-resolved energy spectra of $^{20}Ne^+$ scattered ions
# ($E_0$ = 1 keV, $\theta$ = 120°, $\psi$ = 60°)

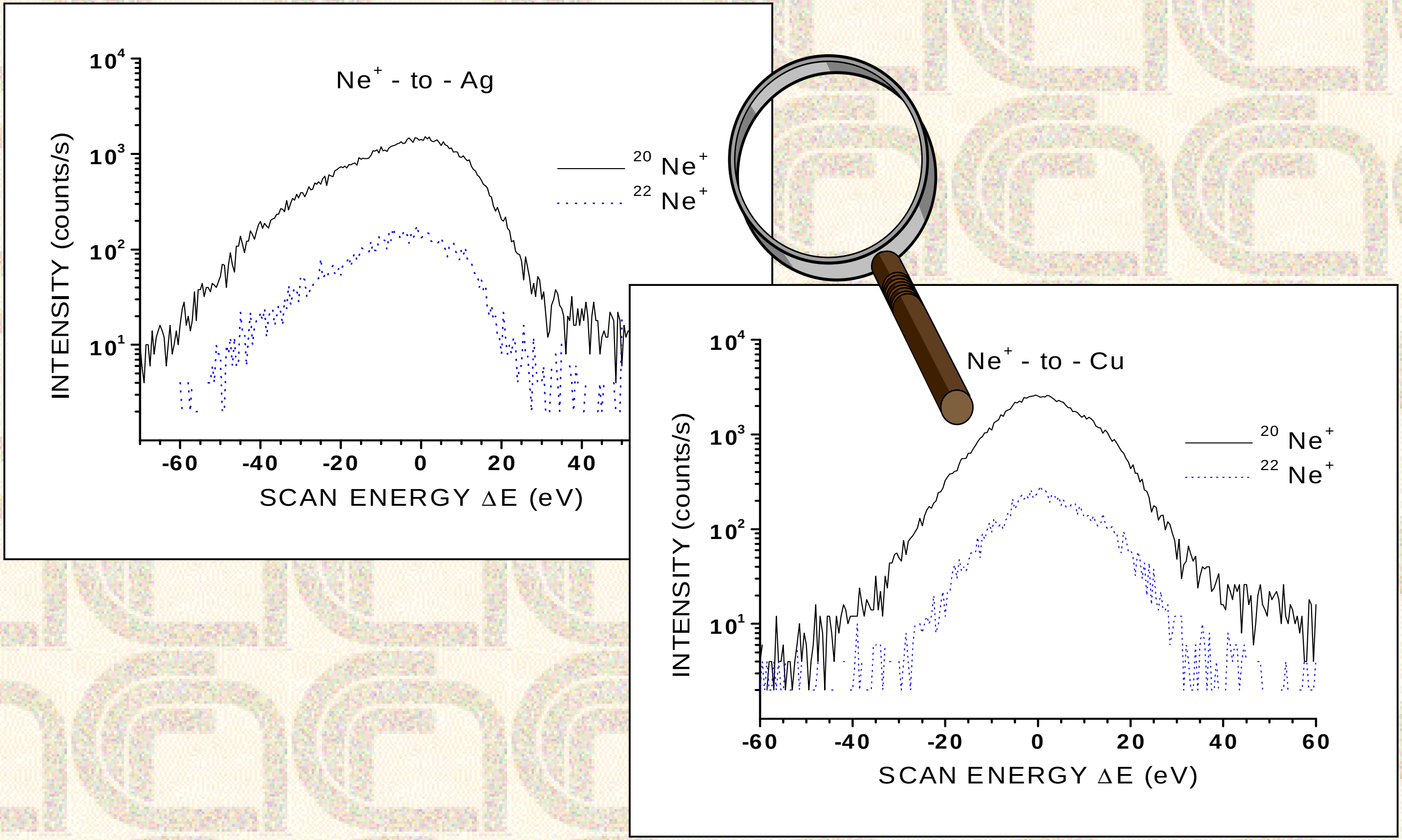




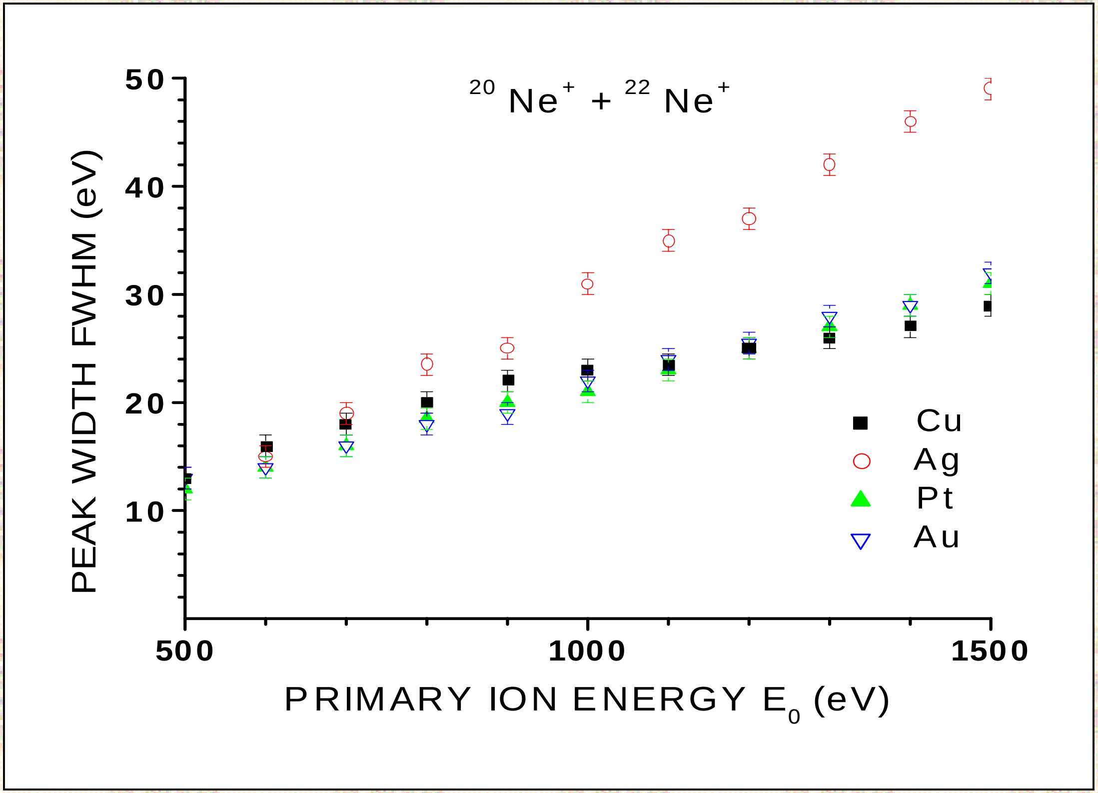




# A close-up view of superposed scans for $^{20}$Ne$^{+}$ and $^{22}$Ne$^{+}$ scattered ions …



# … How the scattered peak FWHM depends on the primary-ion energy



The **ion scattering signal *S*** *(the binary elastic collision peak)*, due to the *i* -component in the surface of the sample, can be written as:

$$S_i = I \cdot P_i^+ \cdot N_i \cdot \sigma_i \cdot F_i \cdot R \cdot \alpha_i$$

- ***I*** is the primary-ion current;
- $P_i^+$ is the **ion-survival probability**;
- $N_i$ is the surface atom density;
- $\sigma_i$ is the cross section per solid angle $\Delta\Omega$;
- $F_i$ is an experimental factor including the analyser transmission and the detector efficiency;
- ***R*** is a correction factor for rough surfaces ($R$ =1 for a flat surface);
- $\alpha_i$ is a steric factor taking into account shielding by neighboring atoms ($0 \leq \alpha_i \leq 1$).

If consider that only the Auger process is dominant, the **ion-survival probability *P*$^+$** is

$$P^+ = \exp(-v_c / v)$$

where $1/v = 1/v_{in} + 1/v_f$ with $v_{in}$ and $v_f$ being the normal components of velocities (Hagstrum) or total velocities (Godfrey-Woodruff) of the ion on the incoming and outgoing (final) parts of the trajectory respectively, and $v_c$ is the **characteristic velocity** (neutralization constant) for the ion-target combination obtained by integrating the Auger transition rate over the length of the projectile trajectory.

The term ***1/*$v$** represents the time that the particle spends near the surface, with **larger** values of $v_c$ leading to a **smaller ion fraction** of the scattered particles.

Assuming that $P^+$ is a function of the reciprocal (inverse) velocities, it has become a custom to plot the natural logarithm of the normalized intensity ***lnS* versus *1/v*** by using the following **experimental approaches**:

- **variation of the scattering angle** at fixed primary energy or **variation of the primary energy** at a fixed scattering angle (*Brongersma et al*.);
- **angular distribution measurements** of ions scattered into the plane normal to that containing the incident beam and normal to the surface of the target with a fixed primary energy and a movable analyser (*O'Connor, MacDonald et al.*);
- **Dual-Isotope Surface Composition technique** (*Brongersma et al, Surf.Sci. 227 (1990) 361*) or **multi-isotope investigation** (*Wittmaack, Surf. Sci. 345 (1996) 110*)

Dual-Isotope Surface Composition (DISC) technique is based on the use of the two (or more) isotopes of the primary ions as projectiles

- ***For a given incident energy $E_0$, the lighter isotope ion has the higher velocity before and after collision;***
- ***The neutralization constant $v_c$ remains the same for all isotopes;***
- ***The apparatus factors and sample characteristics are practically unaltered during dual-isotope scattering ion measurements.***

**Our updated Dual-Isotope method involves the simultaneous use of $^{20}Ne^+$ and $^{22}Ne^+$ as projectiles with additional mass-separation of scattered ions**

By using $^{20}Ne^{+}$ and $^{22}Ne^{+}$ as primary ions, one can finds that

$$\ln\left(\frac{^{20}S}{^{22}S}\cdot\frac{^{22}I}{^{20}I}\cdot\frac{^{22}\sigma}{^{20}\sigma}\right)=\nu_c\cdot\left(\frac{1}{^{22}\nu}-\frac{1}{^{20}\nu}\right)$$

where the upper index of all factors indicates the mass of $Ne^{+}$ isotope ions. It is important to note that:

- **no precise primary-ion current measurements are needed**, because the relative primary current ($^{22}I/^{20}I$) is equal to the natural neon isotopes ratio $k$ = 0.102;

- the differential cross section is practically identical: for ZBL potential **($^{22}\sigma$ / $^{20}\sigma$) = 1.005-1.01** ($E_0$ = 0.5-1.5 keV and $\theta$=120°).

$$\ln\left(\frac{^{20}S}{^{22}S}\cdot 0.102\right)=\nu_c\cdot\left(\frac{1}{^{22}\nu}-\frac{1}{^{20}\nu}\right)$$

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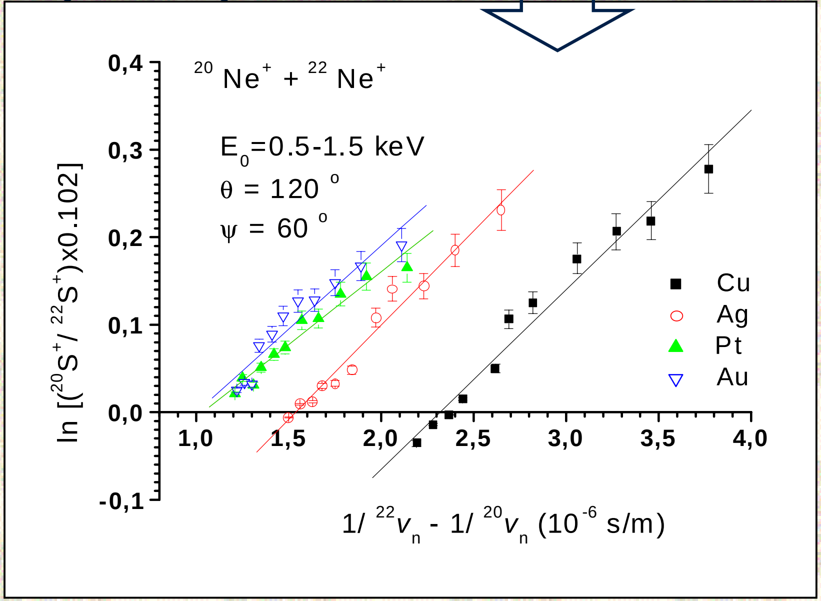
# Plots of the natural logarithm of the peak intensity ratio versus the difference in reciprocal velocities

$$\ln\left(\frac{^{20}S}{^{22}S}\cdot 0.102\right) \approx A + v_c \cdot \left(\frac{1}{^{22}v} - \frac{1}{^{20}v}\right)$$

| | $v_c$, ×$10^5$ m/s | *A* |
|---|---|---|
| Cu | 2.05±0.12 | -0.475±0.033 |
| Ag | 2.15±0.12 | -0.332±0.023 |
| Pt | 1.67±0.10 | -0.173±0.019 |
| Au | 1.90±0.20 | -0.191±0.031 |



Results of linear regression fitting of the experimental data (*for comparison, $v_c$=1.36×$10^5$ m/s for Ne$^+$-to-Au by Buck et al*.)

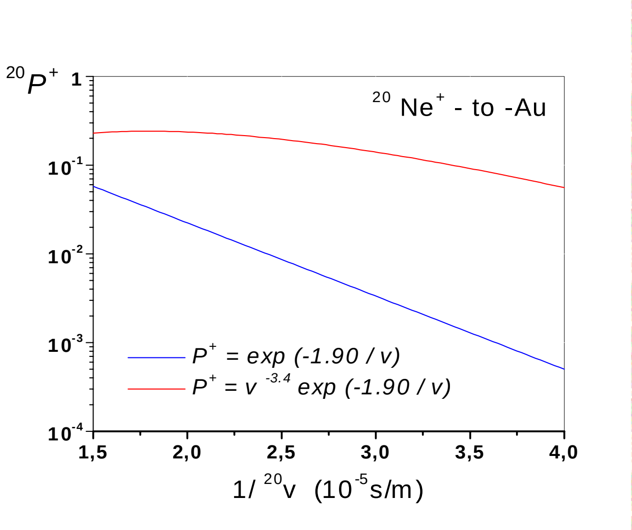
$$P^{+} = (b / v^{n}) \cdot \exp(-v_c / v)$$

where ***b* is the normalization factor** and the index of the power

$$n = A / \ln\left(\frac{^{22}v}{^{20}v}\right)$$

## Projectile parameters estimated for the “critical points”

| *Sample* | *$E_0$, keV* | *$r_0$, Å* | *$^{22}v$, ×$10^4$ m/s* | *$^{20}v$, ×$10^4$ m/s* | *n* |
|---|---|---|---|---|---|
| Cu | 1.3 | 0.37 | 3.344 | 3.632 | 5.7 |
| Ag | 1.5 | 0.41 | 4.129 | 4.401 | 5.2 |
| Pt* | 2.1 | 0.43 | 5.323 | 5.627 | 3.1 |
| Au* | 2.1 | 0.43 | 5.322 | 5.629 | 3.4 |

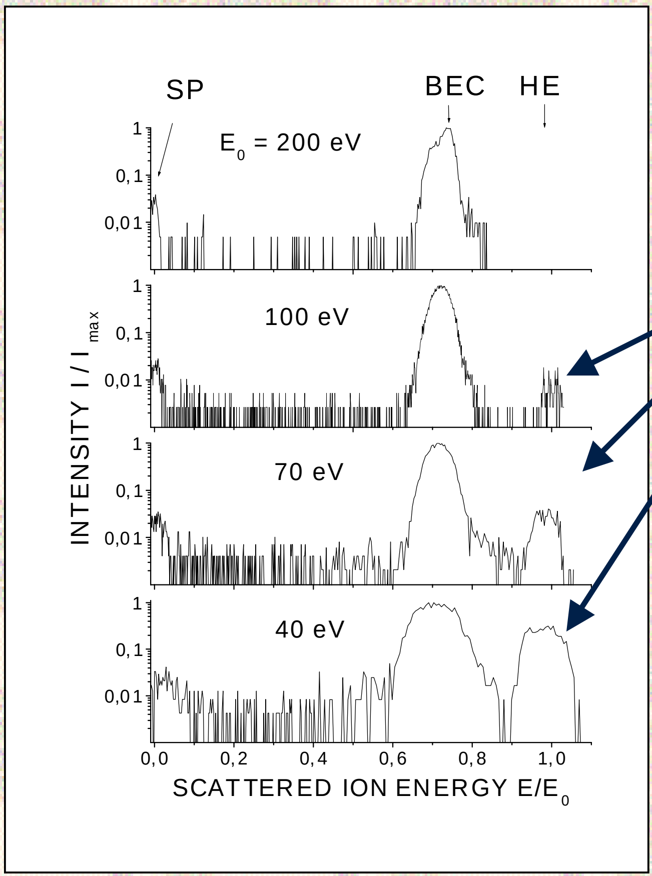


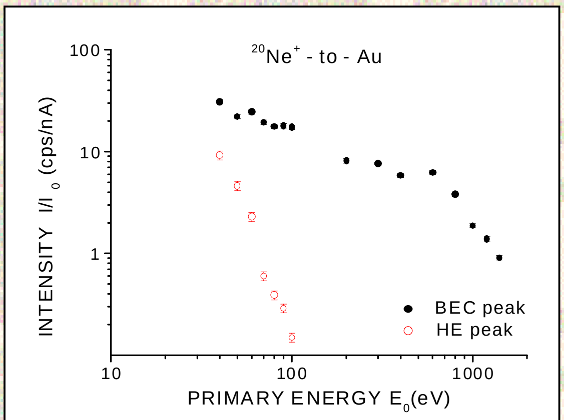
## Ion-survival probability *$P^{+}$* vs the reciprocal velocity

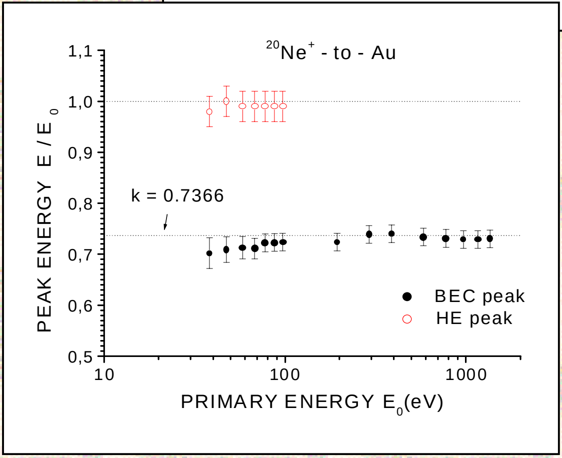
# Conclusions

- *An updated dual-isotope method based on MARISS technique with two isotopes of $Ne^+$ as primary-ion beam was developed.*
- *The data for characteristic velocity $v_c$ for Cu,Ag, Au and Pt were estimated.*
- *An empirical formula for $P^+$ (1/v), containing an additional term dependent on the reciprocal velocity, was suggested without monotone dependence of the ion-survival probability on the reciprocal velocity.*
- *The proposed expression is open to question and call for an adequate physical model based on ab-initio quantum calculation.*

# Hyperthermal energy Ne$^+$ scattering from Au







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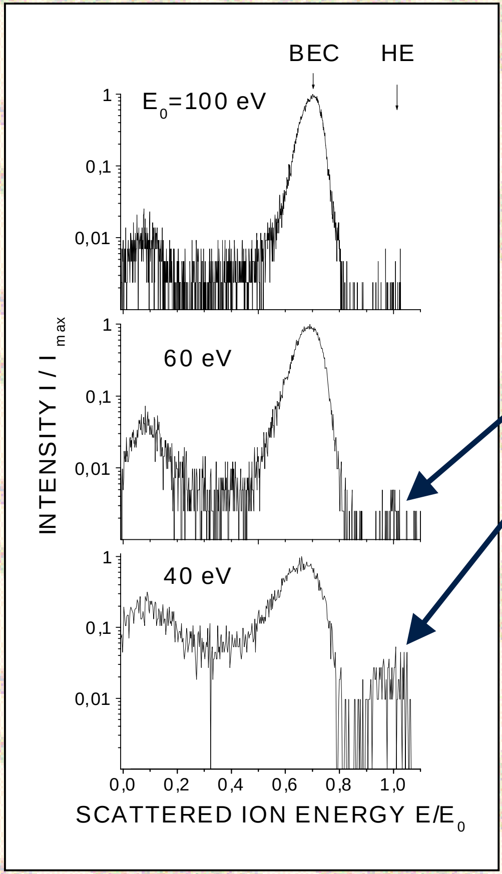
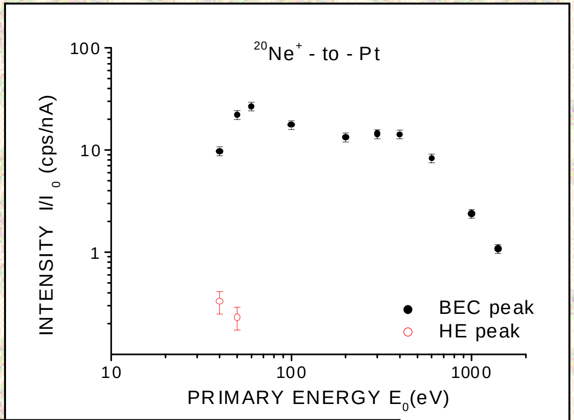
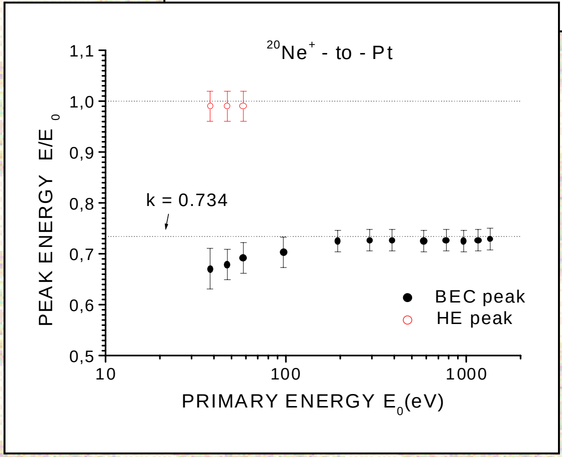
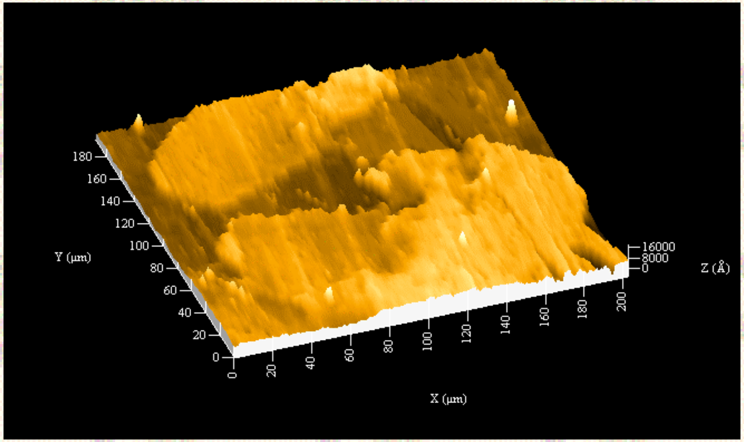
# Hyperthermal energy $Ne^+$ scattering from Pt



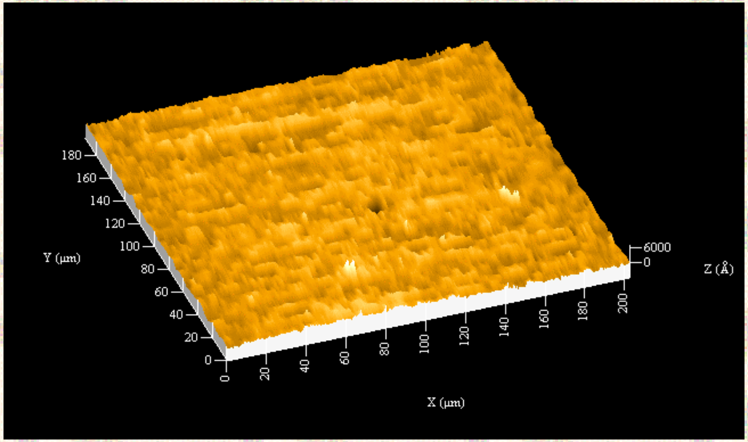




# Surface topography measured after experiments by Tencor Profiler P-10 (a total ion dose was about $10^{16}$ cm$^{-2}$)

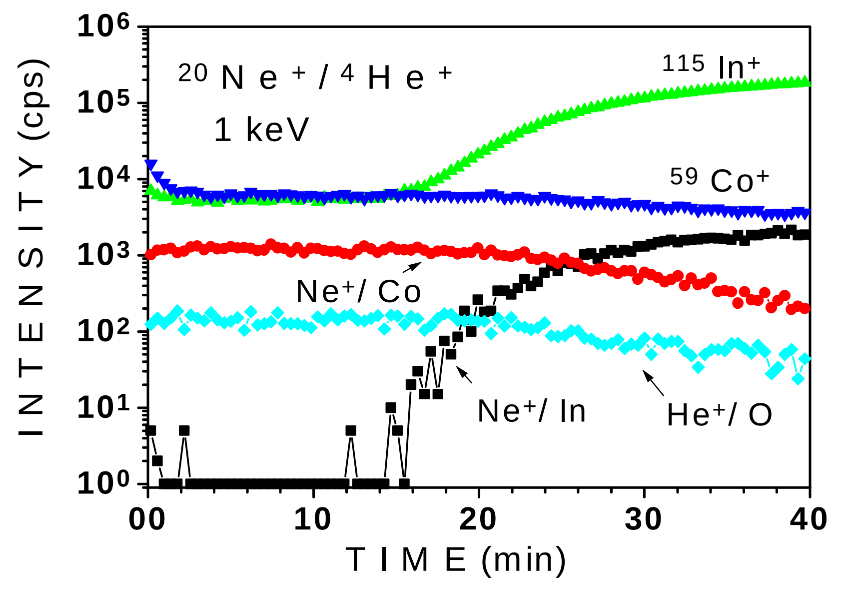


Au sample (*rms roughness is about 210 ± 130 nm*)



Pt sample (*rms roughness is about 92 ± 8.5 nm*)

# SIMS-MARISS depth profiles of cobalt oxide film (about 25 nm) on indium tin oxide (ITO) substrate



Primary ions - Ne$^+$+He$^+$, 1 keV / 1 $\mu$A, $2\times2$ mm$^2$, 20% el. gating, $\theta = 120°$. Peaks of interest: SIMS -$^{115}$In$^+$, $^{59}$Co$^+$; MARISS - $^{20}$Ne$^+$-to-In (596 eV), $^{20}$Ne$^+$-to-Co (352 eV), $^4$He$^+$-to-O (474 eV)

***"Significant items in a given group normally constitute a relatively small part of the total items"***

Vilfredo Pareto,
an Italian sociologist and economist