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Breaking Through the False Coincidence Barrier: Photoelectron Photoion Coincidence Spectroscopy for the Study of Elusive Free Radicals

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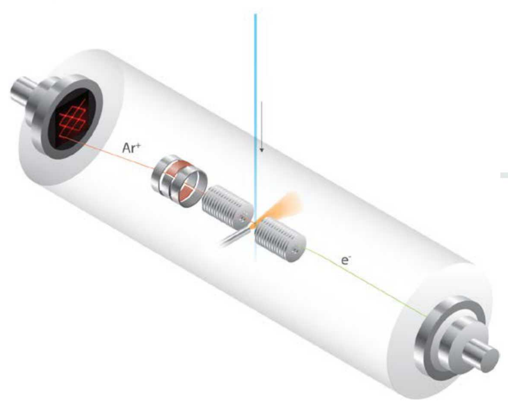
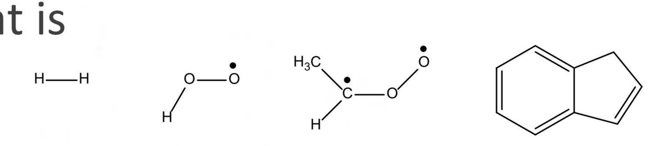
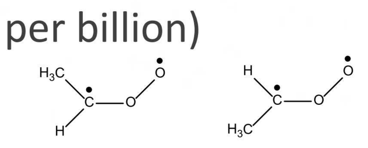
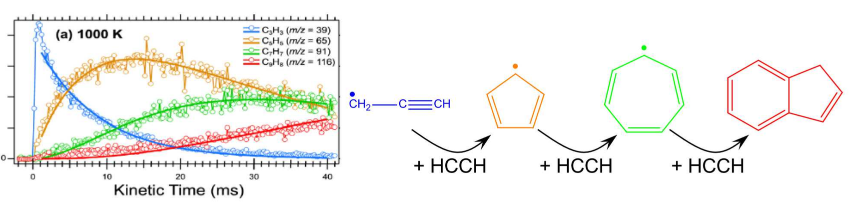


Studying Free Radicals in Bimolecular Reactions

We want a technique that is
- universal
- sensitive (~ 10 parts per billion)
- selective
- multiple
- time-res

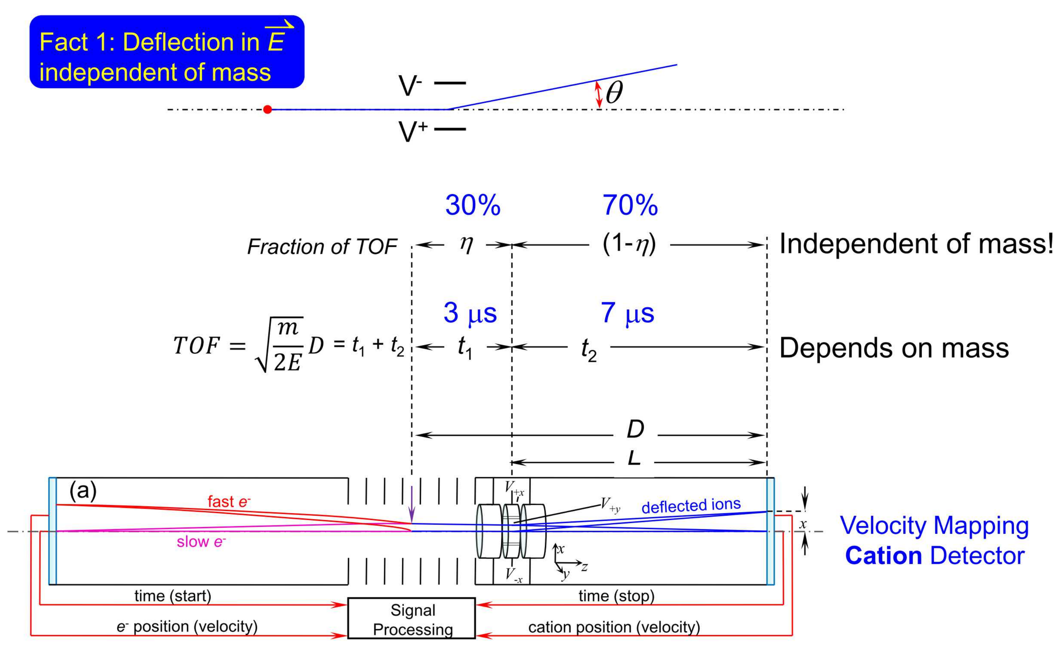






Gas chromatography / Mass Spectrometry ?? → too slow
Multiplexed Photoionization Mass Spectrometry (MPIMS) fulfills (almost) all of these, but…can we do better?

The Key Realization to Identify False Coincidences

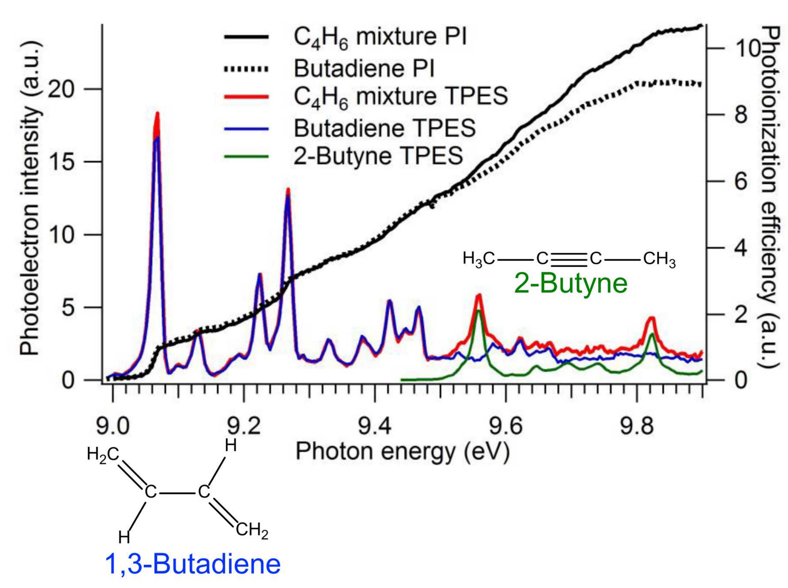


$$TOF = \sqrt{\frac{m}{2E}}\,D = t_1 + t_2$$

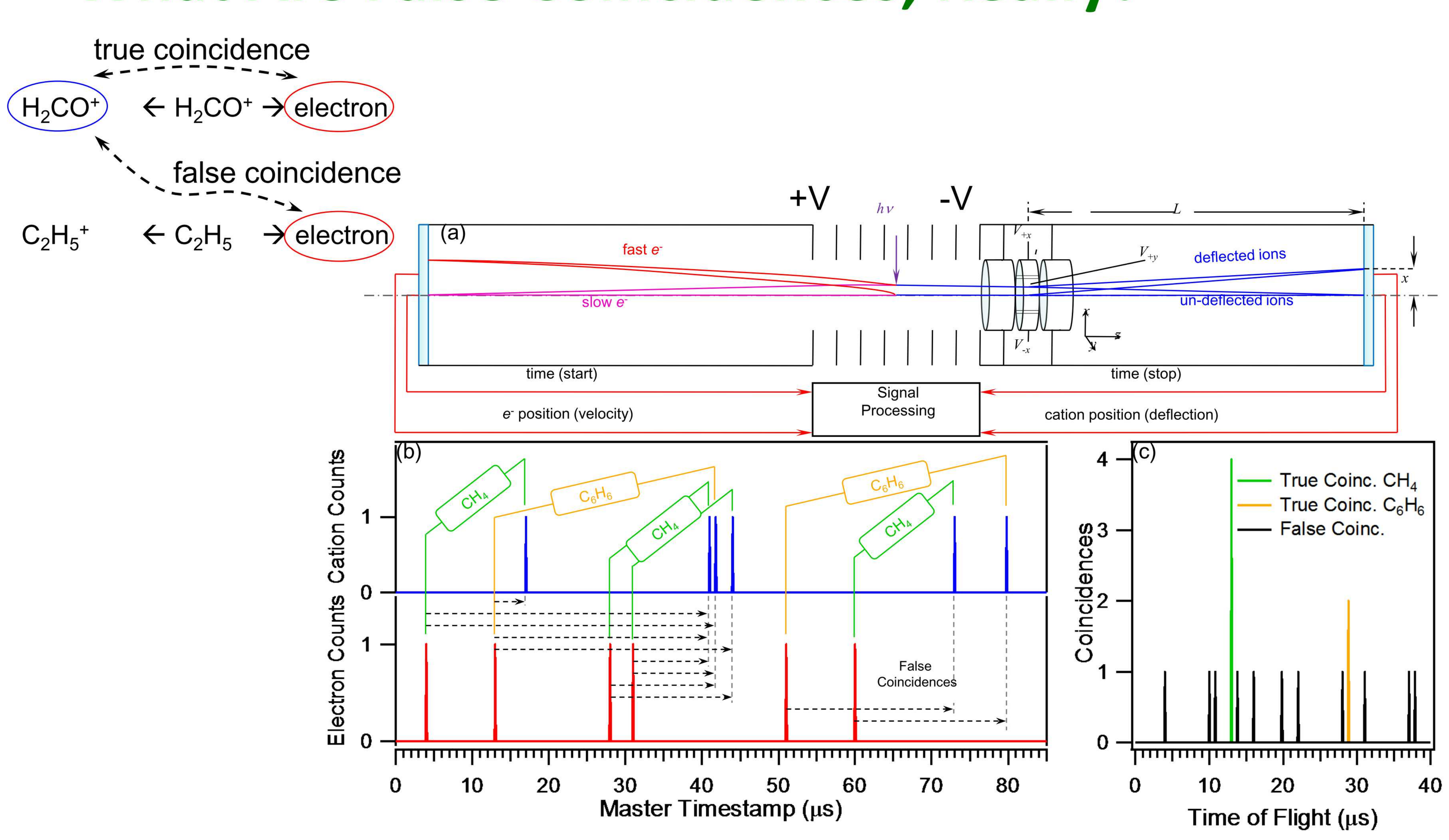
Fact 2: Once η (Fraction of TOF) is determined for an instrument, it is a constant

Photoionization vs. Photoelectron Spectroscopy

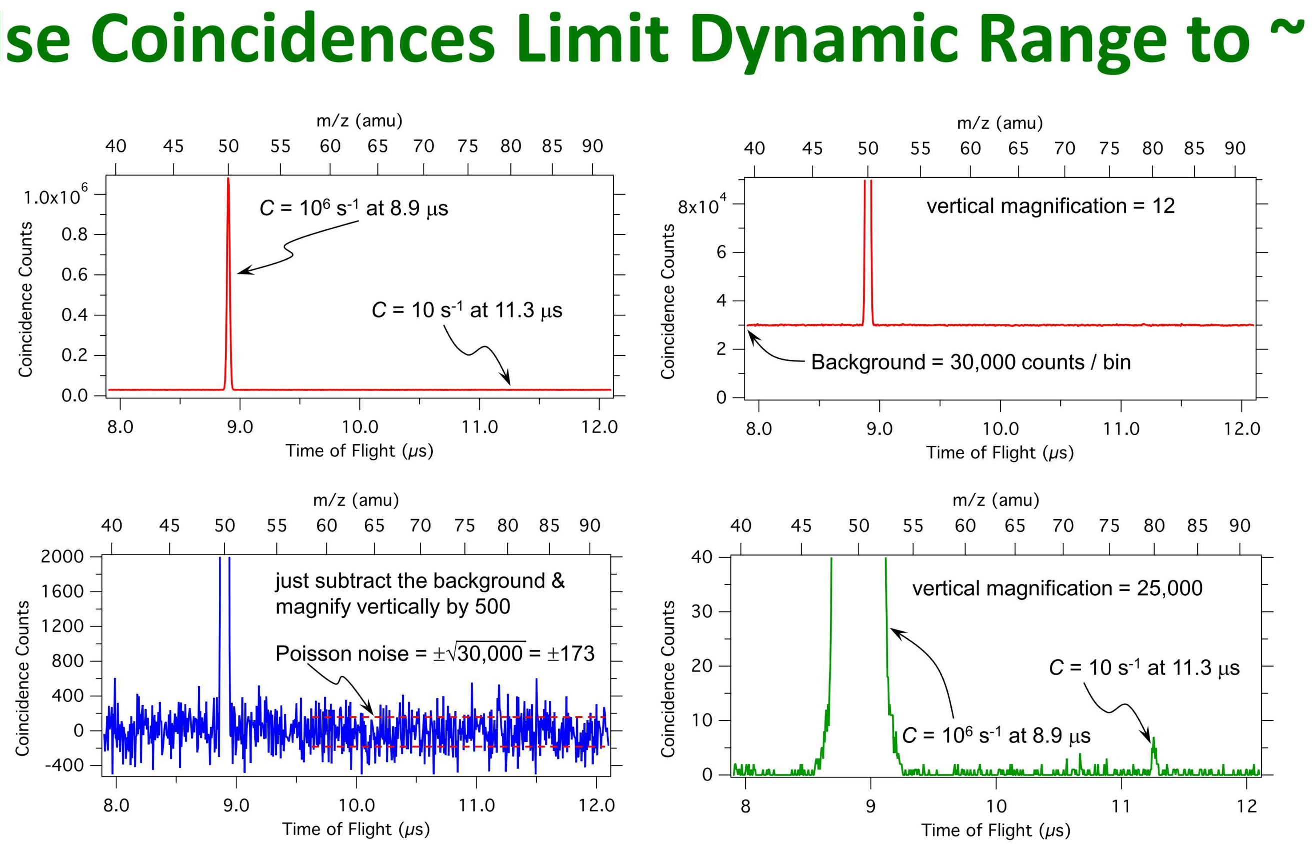
H_2CO	→ H_2CO^+	+ electron
HCO	→ HCO^+	+ electron
CH_3OH	→ CH_3OH^+	+ electron
C_2H_5	→ $C_2H_5^+$	+ electron
	cations have distinct masses	electrons are indistinguishable



What Are False Coincidences, Really?

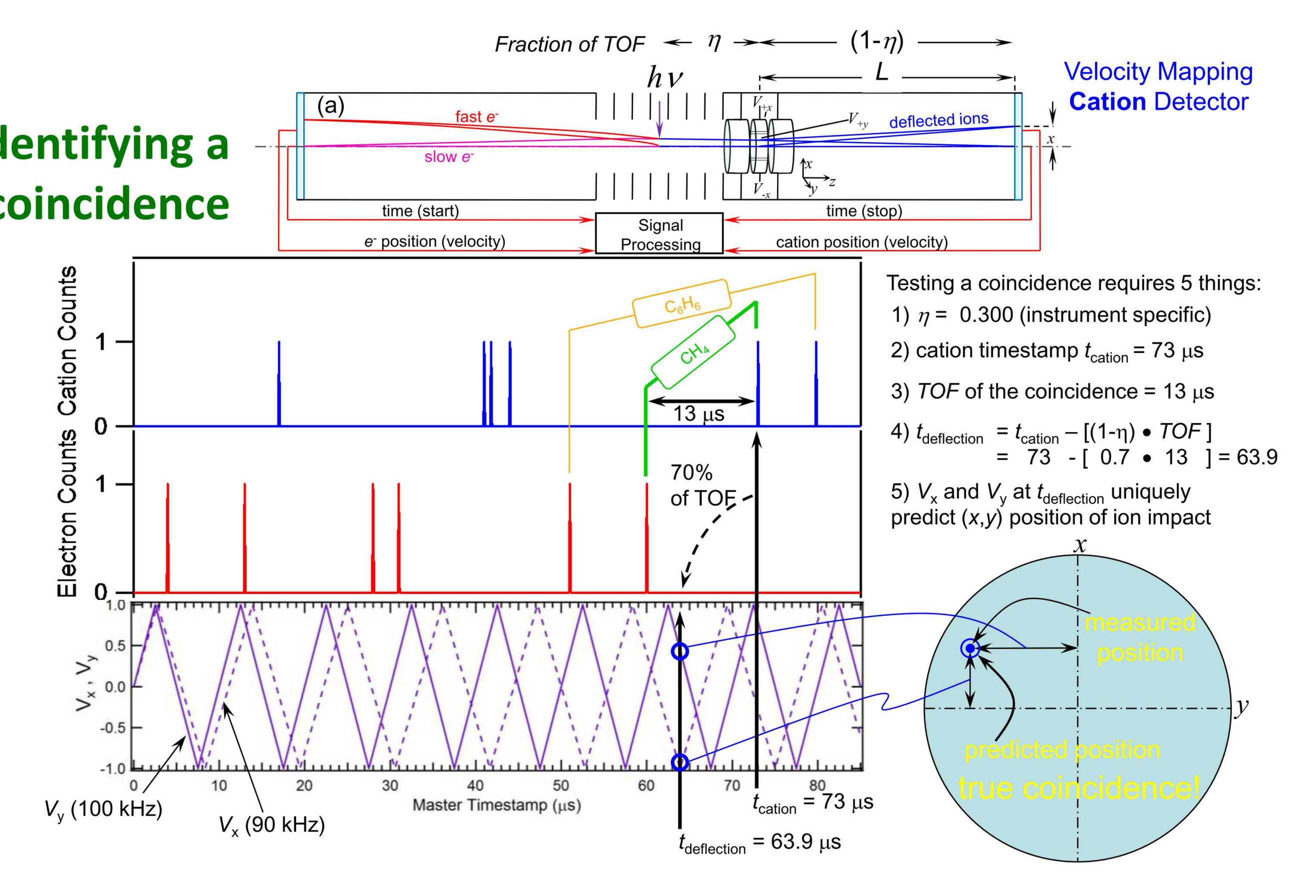


False Coincidences Limit Dynamic Range to ~ 10^3

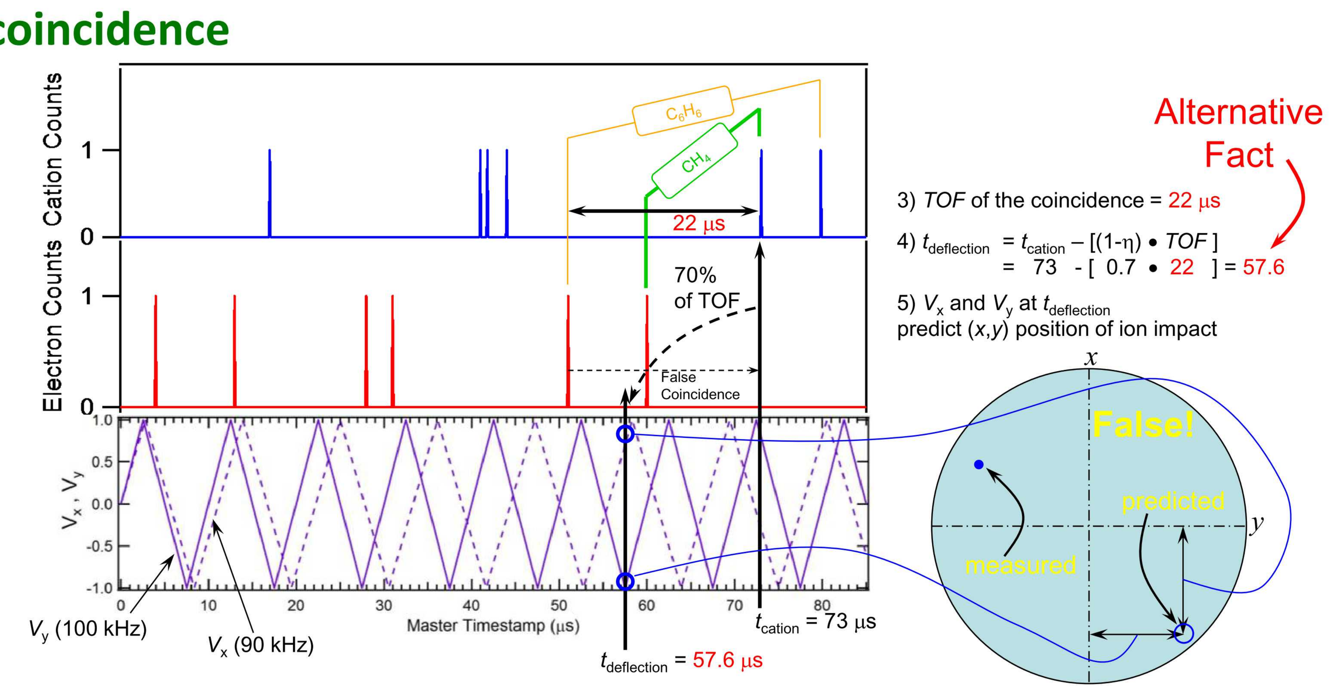


Graphical Explanation of the Method

Identifying a true coincidence

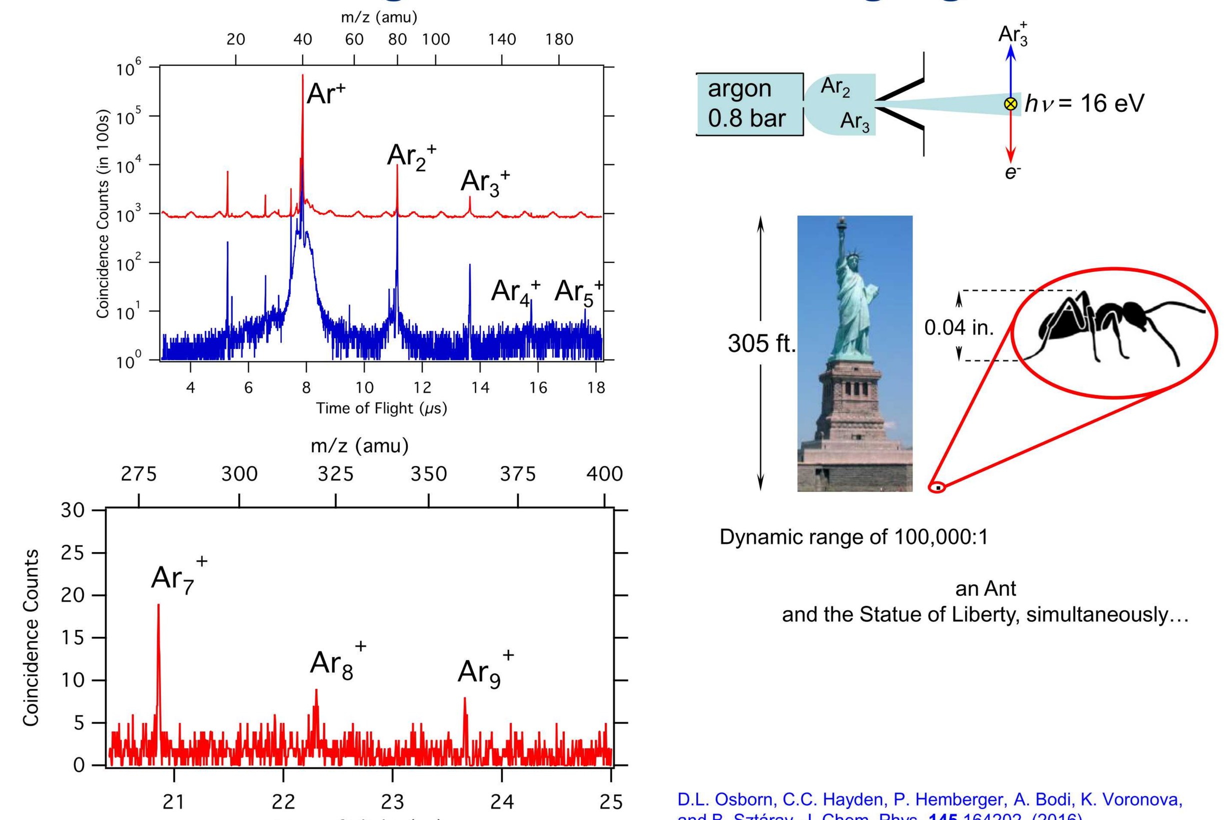


Identifying a false coincidence



An Experimental Test of the Method: Dynamic Range ~ 10^5

Testing the new method using argon clusters



Dynamic range of 100,000:1

an Ant and the Statue of Liberty, simultaneously…

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