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A year in Baltimore

From September 14, 1982 to August 26, 1983 Jean-Claude Tabet was a Visiting Scientist in the Middle Atlantic Mass Spectrometry Laboratory at the Johns Hopkins Medical School. This was the time before MALDI and electrospray, for those of you who remember such a time. In 1978 Kistemaker and coworkers [1] at the FOM Institute in Amsterdam had excited the mass spectrometry world with their mass spectrum of the generally intractable *digitonin* using a pulsed infrared laser and a method which came to be known as *laser desorption*. They used a magnetic sector mass spectrometer, and though the time-of-flight should be considered as the most logical mass analyzer for a pulsed system, the TOF at that time was still regarded as a "toy of fysicists". So other laboratories initially used the instruments available to them. Laser desorption was carried out on sector instruments by Heresch et al. [2] from Vienna and our own laboratory [3], while Vestal and coworkers [4] and Stoll and Röllgen [5] used quadrupoles. The first TOF instruments used for laser desorption were commercial microprobes. Hercules and coworkers at Pittsburgh [6] used a LAMMA 1000 developed in 1975 by Hillenkamp et al. [7].

It was in that context that we assembled the very first TOF mass spectrometer to be used specifically and exclusively for laser desorption [8]. Using a CVC Products (Rochester, NY) mass spectrometer, equipped with an electron impact source and *time-lag focusing*, we added a pulsed carbon dioxide laser and a second delay between the laser and ion extraction pulses, which we called *time-delayed focusing*. While we used this complex ionization/ion extraction pulse sequence to study the time desorption profiles of ions and neutrals (post-ionized by EI), energy spreads and gas phase cationization processes [9], Jean-Claude arrived here principally to advance us into the biomolecule arena.

This was not easy initially. The *jitter* associated with triggering a carbon dioxide laser made it very difficult to align the beginning of the time-delay with the actual laser pulse. And, the long 10.6 micron wavelength did not help, since optical detectors in this wavelength range had a particularly slow response. This means that we were shooting in the dark for quite some time. Those of us in the laboratory during Jean-Claude's first weeks became familiar, day after day, with the audible 1 Hz *ping* of the laser spark circuit from room B5, along with Jean-Claude's responses (in French) reflecting his disappointment. And then (one day) it happened! The excited and repeated cry of "Oh fantastique!" brought us all running. Only those who understand that Jean-Claude is normally in some higher excited state can appreciate his wildly enthusiastic response to his success!

Jean-Claude did go on to look at many biological molecules. In 1984 we published a summary of their spectra in Analytical Chemistry [10]. We found that IR laser desorption worked best when we added a potassium salt to produce the MK^+ ion. We found that focusing was very much dependent upon the time delay between the laser pulse and extraction of the ions, what is now called *delayed extraction*. We also found that we could use the laser power to control fragmentation, and that the amount of fragmentation observed in the mass spectrum depended upon the length of the delay time, today known as *in-source decay*. For peptides, fragment ions could be used to produce the amino acid sequences. In 1983 we did not know exactly what to call these, but in Fig. 1 *Leu-Trp-Met*$^+$ and *Leu-Trp-Met-Arg*$^+$ are today known as *b*-ions.

Peptides were not the only analytes that Jean-Claude studied. We had determined early on that the gas-phase cationization of desorbed neutrals that characterized the IR laser desorption mechanism was particularly advantageous for sugars and lipids [11,12]. Thus, we were able to characterize a series of oxygen-linked glucuronides [13] and to obtain IRLD mass spectra for glycolipids including trehalose fatty acyl derivatives and lipid A from gram-negative bacteria, such as *Salmonella typhimurium* [10]. In addition, we used the time-delay feature of this instrument, in a collaboration with Jerry Hunt at Argonne National Laboratory [14], to follow the metastable decomposition of chlorophyll and several of its derivatives.

There is no doubt that his *year in Baltimore* was an extraordinarily productive one from this very energetic scientist to whom we now dedicate this volume of the International Journal of Mass Spectrometry.

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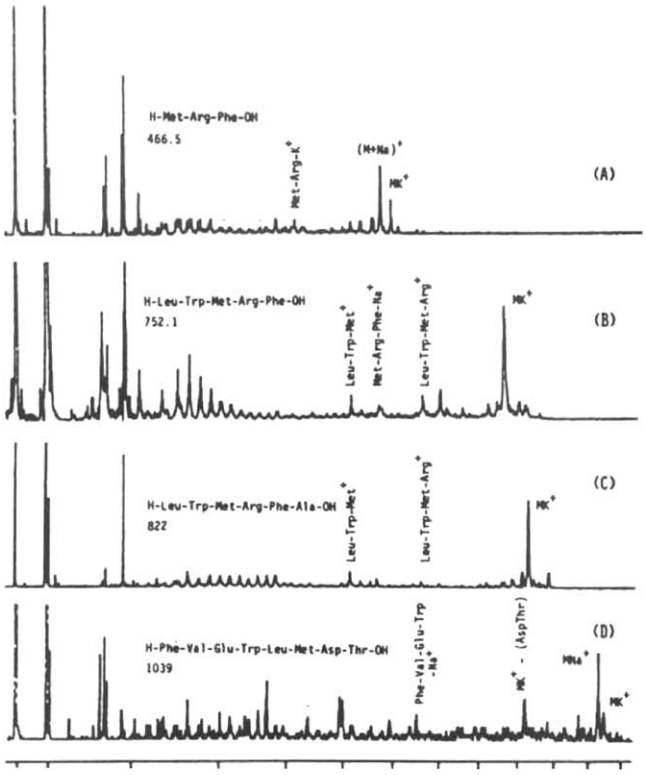

Fig. 1. IR laser desorption mass spectra of several peptides. Reprinted with permission from Ref. [10].

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