Editorial:
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Chemical Ionization Mass Spectrometry: 50 Years On.

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Mass spectrometry (MS) has a rich history of innovations that have transformed its reach into many areas of science, engineering and medicine. Since a prerequisite for MS analysis is the production of gas phase ions derived from the analyte(s) of interest, arguably the invention of new ionization methods has had the biggest impact in overcoming previous limitations and broadening the classes of compounds that can be analyzed via MS. This year is the 50th anniversary of the publication of Munson and Field's seminal paper of Chemical Ionization Mass Spectrometry (CIMS) [1]. While the field of CIMS has been comprehensively surveyed in a book [2] and historical developments have been discussed in several reviews [3-6], some aspects are briefly considered here.

After World War II, the petroleum and chemical industries in the USA were a hotbed of innovation in MS [7], with researchers such as McLafferty (at Dow Chemical, Michigan) and Meyerson (at the Standard Oil Co., Indiana) leading the charge to understand how fragment ions are formed under electron ionization mass spectrometry (EI/MS) conditions. While ion-molecule reactions (IMRs) have a long history in MS, dating back to Sir J. J. Thomson's observation of H_3^+ [8], prior to the 1950s IMRs were regarded as both a curiosity and a nuisance and were known to occur when ion sources were operated at higher pressures. It was the fundamental studies of gas-phase IMRs by Tal'roze [9], Stevenson and Schissler [10] and Field et al. [11] in the 1950s that laid the foundation of CIMS. As noted in Munson's accounts [3,4] instrumental development was a key enabler of CIMS. Thus a mass spectrometer was designed and built at the Humble Oil and Refining Co. Research Laboratories (Baytown) to specifically operate at high source pressures. This allowed Franklin, Field and their colleagues to study ion-molecule reactions at different pressure regimes. In 1959 Munson joined the Research Division of Humble Oil and Refining Co. [5]. After working on other projects, he transferred to Franklin and Field's lab in 1961 to carry out fundamental research on IMRs at "ultra-high" pressures of 0.1-0.3 Torr [6]. During studies on ion formation in methane, Munson and Geiger found that the types of ions observed in the mass spectra were dependent on ion-molecule reactions between ions derived from methane with trace impurities [5]. By eliminating these impurities they established that CH_5^+ [12] and C_2H_5^+ formed in methane do not further react with methane. This set the stage to study the reactions of these ions with additives, giving rise to the development of CIMS.

The essential aims of Munson and Field's seminal paper on CIMS are succinctly summarized in their introduction [1]:

"The purpose of this paper is to present a new technique of generating mass spectra, chemical ionization mass spectrometry, in which the characteristic ionization of the

materials in question is produced by ionic reactions rather than electron impact. These chemical ionization mass spectra will probably be of particular interest for analytical mass spectrometry.”

CIMS, electrospray ionization and desorption electrospray ionization represent examples of innovations in mass spectrometry that have been met with skepticism by reviewers unable to appreciate their significance. Munson has recounted that their first CIMS paper received the review *“I think that one should give serious consideration to the value of the work and the usefulness of publication”* [4]. Fortunately, through the dogged determination of their inventors, these techniques are now well established, have powered the growth of our discipline and received the attention and recognition they deserve. In the case of CIMS, Munson received the American Chemical Society’s Frank H. Field and Joe L. Franklin Award for Outstanding Achievement in Mass Spectrometry in 1992, and Munson and Field were recipients of the ASMS Distinguished Contribution in Mass Spectrometry award in 1996.

On a final note, it is fitting on this anniversary for *JASMS* to publish a paper by Newsome, Steinkamp and Giordano on the development of an isobutane-argon CI mixture for more robust CIMS [12]. Munson recently stated that *“CIMS is a well-established technique – “old hat”, these days”* [4]. Apparently, even the classics can be refreshed and improved.

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