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Foreword

Editor's personal foreword

One of the great things about being the Special Issues Editor for IJMS is the opportunity to pick topics and Guest Editors for the Special Issues. When the Editorial Board began discussions on how to honor J.J. Thomson as the 100th anniversary approached of his game-changing book "Rays of Positive Electricity", published in 1913, we were not sure how to accomplish it. We knew we could not do it in one issue. Then I got an email from Klaus Blaum of the Max-Planck-Institut für Kernphysik in Heidelberg, Germany. Klaus proposed to do a Special Issue on Thomson that covered mass measurement advances of the past 100 years. He proposed articles of both a historical bent and those more focused on how Mass Spectrometry has benefited Nuclear Physics, his area of expertise. I jumped at the idea because it provided a solution to the conundrum we were facing. It would provide an issue true to Thomson's roots and provide essentially no overlap with the idea that became the focus of this Special Issue. It also allowed us to publish an issue in 2013, the 100th year anniversary of Thomson's book. Klaus recruited Yuri Litvinov of the Helmholtz Research Center in Darmstadt, Germany to co-edit the SI and the Issue was published as volumes 349 and 350 of IJMS in September 2013. Publishing this SI in 2013 provided us time to organize this current, broader based issue focused on the development of Mass Spectrometry applied to Chemical (and now heavily Biochemical) problems.

I had a vague idea it would be best to focus on the last 50 or so years as that era has experienced the explosion of Mass Spectrometry in the Chemical Sciences. I knew I needed assistance in this effort to get it right and I was extremely fortunate that when I asked Jean Futrell to be a co-Guest Editor he enthusiastically agreed to do it. Jean has been at the forefront of instrument development for 50 plus years, his scientific and leadership credentials are impeccable, and his knowledge of the people and the nitty gritty details of Mass Spectrometry encyclopedic. And as a bonus when I asked him to tell his scientific story as a part of this issue he was willing to take that on as well. It appears as a special Foreword following this one. As Jean and I brainstormed on how to put the issue together we felt there were natural divisions in the field that should be emphasized and special people that could hopefully be recruited to do retrospectives on topic areas that fit within the Special Issue concept. We hoped to surround each retrospective with 4 or 5 current research topics that grew out of the earlier work described in the retrospectives. More on this point in the General Foreword that follows this one.

We recently lost two giants in our field in Nico Nibbering and Franz Hillenkamp, both of whom died in August 2014. We are very fortunate, privileged and honored to have Nico's final scientific contribution in this SI; his retrospective on "Highlights of 50 years of ionic reaction mechanism studies". Unfortunately we were not able to get a paper from Franz. However both Nico and Franz will be individually honored with Memorial Issues that are already in the planning stages. Enjoy this classic Issue. There really is nothing else like it.

Michael Bowers
Santa Barbara, CA, USA
September, 2014

General foreword

In this Special Issue of the International Journal the Editors have attempted to identify major breakthroughs in instrumentation and concepts that originated in the time frames of their own professional careers and are having, or are projected to have, major impact on the molecular sciences—chemistry, biology, medicine and environment—in the next half century. We were encouraged to undertake this effort by the celebration by our community of the founding of the field of mass spectrometry a century ago by J.J. Thomson in his Baker Lecture and subsequent publication of his monograph *Rays of Positive Electricity* in 1913 that identified the positive charge carriers in an electric discharge as singly and multiply charged atoms and combinations of atoms. [For context, in 1914 Henry Ford introduced assembly line manufacture of automobiles in the United States and World War I began in Europe.] In the second edition of his monograph, published in 1921, Thomson made the remarkable prediction, "Another subject on which Positive Rays may, I think, be expected to throw light is that of the structure of the molecule. For, as we have seen, when a compound gas is in the discharge tube there are among the positive rays not only the individual atoms which went to make up the molecule, but also unsaturated combinations of these atoms. The proportion in which these combinations are present yields information about the configuration of the molecule." The realization of this prescient prediction is the collective theme of this Special Issue.

Major progress toward realizing this prediction was delayed until the years following World War II, which sparked remarkable advances in vacuum tube electronics, oil diffusion pumps and related vacuum technology and other advances largely connected to the Manhattan Project to develop the atomic bomb. Prior to these wartime advances the creation of new instruments demanded "tour de force" efforts to fabricate ion sources, mass

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analyzers and detectors. The first commercial mass spectrometer, originally conceived for examining soil and drilling core samples for traces of oil, was the Consolidated Engineering Corporation model 21-101, first installed at Atlantic Refining Company in Philadelphia in 1943. [Timeline, Battle of Stalingrad (St. Petersburg) reversed the tide of Nazi victories in WW II.] Because it provided catalytic cracking operators relatively rapid data, this instrument—based on Dempster's invention of a direction-focusing magnetic deflection mass analyzer at the University of Chicago in 1918—was of enormous help to the Allies in maximizing the production of high-octane aviation gasoline for the air war in Europe.

What we hesitantly describe as the "modern era", beginning in the 1960s, represents the time frame in which several examples of the key components—ion sources, mass analyzers and detectors—were known and it was possible to think of addressing problems in molecular structure, chemical reactivity and composition utilizing mass spectrometry as a key research tool. Advances in the 1950s made this an auspicious time to launch careers in mass spectrometry. Consolidated Engineering Corporation changed its name to Consolidated Electrodynamics Corporation and introduced its updated 21-103 Dempster type mass analyzer with unit resolution over its mass range of 1–150 in 1950. Al Nier and W.H. Johnson designed a double-focusing "high resolution" mass analyzer at the University of Minnesota in 1952. In the same year Henry Eyring, Austin Wahrhaftig and their students, Henry Rosenstock and Merrill Wallenstein, developed the fundamental theory relating mass spectra to molecular properties and Victor Tal'rose in Moscow re-discovered ion molecule reactions and measured their rates—establishing them as the fastest known chemical reactions. [Timeline: US tests first Hydrogen Bomb and first commercial jetliner enters service.] Bendix introduced the Time-of-flight mass analyzer in 1958 and Fred McLafferty and colleagues at Dow Chemical demonstrate the remarkable utility of combining such a rapid scan instrument with gas chromatography. In 1961 CEC introduced its first high resolution mass analyzer, a double-focusing mass spectrograph first described by J. Mattauch and R. Herzog in 1934. This updated instrument utilized two detectors, the glass photographic plate for recording the full mass spectrum (without scanning) similar to that utilized in the 1934 instrument and an electron multiplier detector for high sensitivity detection at a selected mass. For this detector the full high resolution mass spectrum was obtained by scanning the accelerating and electric sector voltages. [Timeline: Yuri Gagarin orbits the earth as the first space astronaut.] Mass spectrometry was rapidly evolving on a path to becoming what it is today—an invaluable analytical tool for chemistry and the molecular sciences.

With this backdrop we have organized the papers in this Special Issue in broad categories of Instrumental Innovations, Advances in Ionization, Analytical Chemistry Applications, and Ion Chemistry. Each of these broad categories is further subdivided into topics related to different directions taken by mass spectrometry relating to either technological advances or evolving research objectives. We have invited a number of leaders of a certain age to write retrospective papers that describe the origin and evolution of a part of the ever-expanding continuum of mass spectrometry from their personal perspectives. These are accompanied in most cases by invited research papers that describe current topics and their logical projection into mass spectrometry's Second Century. In all there are 77 papers in this issue that span the width and breadth of Mass Spectrometry. We hope you enjoy reading it as much as we enjoyed putting it together.

Jean Futrell
Richland, WA, USA
August, 2014

Michael Bowers
Santa Barbara, CA, USA
August, 2014

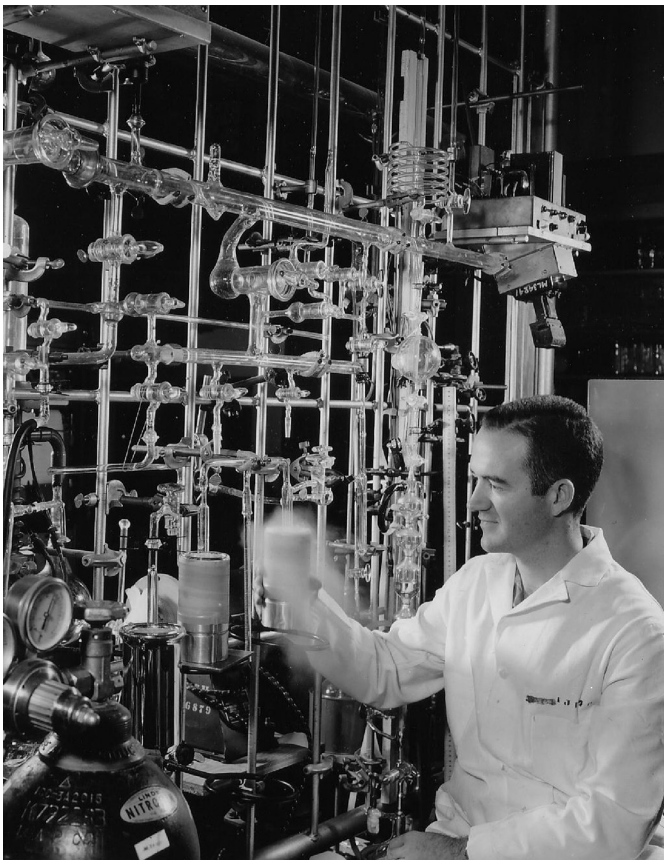

Fig. 1. Radiation chemistry graduate student Jean Futrell practicing bulb-to-bulb distillation separation of radiolysis products for mass analysis at the Lawrence Berkeley Laboratory in 1956.

Guest editor Jean Futrell—my story

As a radiation chemistry graduate student at the Lawrence Berkeley Laboratory in 1955–1958. I had my first encounter with mass spectrometry as an analytical instrument. Fig. 1 shows the author as a first year graduate student practicing state-of-the art bulb-to-bulb separation of volatile gas samples into several—typically five—fractions for analysis using the newly-acquired CEC 21-103 mass spectrometer at LBL. These fractions were submitted to the MS technician who returned to me the next day scrolls of photographic paper recording mirror deflections of an optical signal at 5 different sensitivities of electrometer signals obtained as the accelerating voltage of the spectrometer was scanned—the precious mass spectra of my unknown products. He also provided me a scroll of background peaks obtained with the same spectrometer that included mercury isotope peaks—originating from the mercury diffusion pump on the analyzer tube—as an absolute mass calibration. This approach worked remarkably well for fixed gases—hydrogen and methane—and for volatile gases whose spectra were well known but failed for complex mixtures of less volatile non-hydrocarbon compounds.

What was clearly needed was an improved separation procedure and the technique that I adopted was gas chromatography (GC) which seemed to offer the solution to my problem. The core analytical method that I adopted was a combination of gas chromatography (GC) and mass spectrometry (MS)—not GC/MS, which was developed much later. Gas chromatography had been developed in Great Britain as an analytical chemistry method but had not matured as a commercial product. With fabrication of the requisite packed column filled with thinly coated, uniform size particles as