

Go with the flow: Fifty years of innovation and ion chemistry using the flowing afterglow



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ABSTRACT

This retrospective chronicles the invention of the flowing afterglow technique fifty years ago by Ferguson, Fehsenfeld, and Schmeltekopf at the National Bureau of Standards Laboratories in Boulder, Colorado. Their pioneering development and applications of this powerful new experimental approach to a multitude of atmospheric reactions are described. The implementation and extension of the technique by scientists throughout the world is briefly discussed, and the paper concludes with a more personal story of research and innovation at the University of Colorado.

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1. Introduction

The field of mass spectrometry is deeply rooted in physics, but it has truly blossomed in the realm of chemistry. The study of gas phase ion chemistry has a long and illustrious history; indeed, the first laboratory detection of ion–molecule reactions was made by Sir J.J. Thomson [1] in his observation and insightful identification of H_3^+ in a hydrogen discharge tube. The complete title of his classic work “Rays of Positive Electricity and their Application to Chemical Analysis” published in 1913, reveals his early appreciation of the potential profound impact of mass spectrometry on the chemical sciences and on gas phase ion chemistry.

In the succeeding decades, the existence of gaseous ions was documented in many environments including the interstellar medium, the Earth’s atmosphere, plasmas, and flames. It was recognized that elucidating the relevant gas phase ion chemistry could provide unprecedented insight into these regimes, as well as into physical organic chemistry, catalytic processes, combustion, and biological systems, among many other interdisciplinary areas. Nevertheless, if we “fast-forward” 50 years from Thomson’s classic discovery, we would find that gas phase ion chemistry was still in its infancy, and that for example, “no single atmospheric ion–molecule reaction rate constant was unambiguously determined!” [2] This unfortunate situation was largely due to the

nature of the laboratory instrumentation, which had extremely limited capabilities for investigation of chemical kinetics.

However, if we could peer into the labs and offices of the National Bureau of Standards (NBS) in Boulder, Colorado, in 1963 we would see the triumvirate of young physicists shown in Fig. 1. Eldon Ferguson, Art Schmeltekopf, and Fred Fehsenfeld dramatically changed the status quo by developing a powerful and versatile technique known as the flowing afterglow. Eldon came to Boulder in 1962 from the University of Texas–Austin to create a program in laboratory aeronomy; he was soon joined by his two gifted graduate students, Art and Fred. In the words of Eldon, “The invention of the flowing afterglow was, like much of science, more a matter of serendipity than of judiciously calculated planning.” [2] While waiting for the completion of their lab space, Art spent a month with Herb Broida at NBS in Washington, studying optical spectroscopy in a flow-discharge system; they detected emission from excited ions and neutrals which persisted throughout the length of the flow tube. This surprising observation suggested the intriguing possibility that reactions of ions could be studied and characterized in these devices; and so in Boulder, Eldon, Art and Fred built the first flowing afterglow apparatus, and thereby initiated an era of unrivaled productivity and progress.

The original instrument [3], shown in Fig. 2, employed a pyrex flow tube about 8 cm in diameter and 100 cm in length in which ions are generated and their reactions carried out, and a differentially-pumped detection system. The key diagnostic was a quadrupole mass filter, recently invented by Wolfgang Paul [4], which provided mass analysis of the ions. In a typical

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Fig. 1. Left to right: Art Schmeltekopf, Eldon Ferguson, and Fred Fehsenfeld in 1963 at the NBS Labs in Boulder.

experiment, a large capacity Roots blower pumps helium buffer gas through the system at a pressure of about 0.5 Torr and a flow velocity of about 100 m/s. The helium is excited and ionized by a discharge or by a variety of other methods at the flow tube entrance, and traces of reactant gases are added to transform the initial ions to the desired reactant ions. The reactant ions are allowed to flow about 30 cm before addition of a neutral reactant gas, so that they undergo many collisions and are thermalized. The neutral reagent is then added through a fixed or movable inlet and the ion–molecule reaction occurs from the point of addition of the reactant to the point of sampling of the plasma. Multiple inlets and reactants can be employed to carry out a complex sequence of reactions. Most of the gas flow is pumped away by the Roots blower but a small fraction is continuously sampled through an orifice on the flow tube axis; the ions are focused, mass analyzed, and detected. Rate constants can be readily determined by measuring the reactant ion intensity as a function of neutral reactant flow (with a fixed inlet) or as a function of reaction distance (with a movable inlet). Reaction products and branching ratios are identified by monitoring the evolution of the total mass spectrum as the reaction proceeds. Fig. 2 schematically includes green, pink, and blue afterglows to illustrate the visible emissions that were often produced and analyzed to further characterize the reactants and products. Although spectroscopic analysis is not common in current studies using the flowing afterglow method, the colorful designation of the technique remains. This drawing of the original instrument graced the walls of the NBS labs for many years, and was used in many scientific presentations.

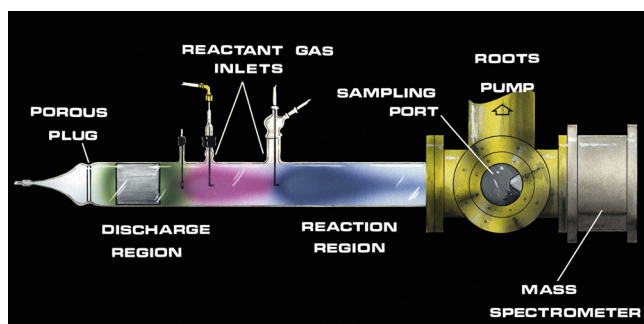


Fig. 2. The original flowing afterglow instrument. Reprinted from V.M. Bierbaum, instrumentation: flow tubes, in: P.B. Armentrout (Ed.), *Encyclopedia of Mass Spectrometry*, Elsevier, Amsterdam, 2003, pp. 98–109.

Zdenek Herman, a close colleague and discerning artist, provided a second schematic of the flowing afterglow (Fig. 3), which reveals its secret subterranean community. As seen by a visitor to the lab on the upper panel, the flowing afterglow is a very simple device. But Zdenek recognized that the true scope and power of the instrument is hidden in the basement below! The enormous pumps provide the high flow velocities, while the racks of cylinders supply the large quantities of helium. And most importantly, the strong, industrious graduate students make the experiments possible – an apt metaphor!

The flowing afterglow technique incorporates several valuable features that allowed it to revolutionize studies of ion chemistry: (1) The quadrupole mass filter provides definitive identification of the reactant and product ions. (2) The ion formation and reaction regions are spatially and temporally separated. The reactant ions are collisionally relaxed before reaction, and the neutral reactants are added downstream of the ionization region. Therefore, both the ionic and neutral reactants have well-defined thermal energy distributions. (3) As will be described below, energy variability is possible; the flow tube can be heated or cooled for temperature-variable studies, and a drift tube can be incorporated for studies as a function of kinetic energy. (4) Because of the interrelationship of distance and time in a flow system, kinetic measurements are straightforward. Detailed hydrodynamic analysis indicated that the helium flow is well-characterized [3]. (5) The technique provides high ion densities and good sensitivity, so that alternate source technologies (for example, the selected ion flow tube) and detection methodologies (for example, laser-induced fluorescence and infrared chemiluminescence) can be implemented. (6) Exceptional chemical versatility is possible. A wide array of positive and negative ions can be formed by an arsenal of ionization methods, and a large variety of neutral reagents, including radical and highly reactive species, can be generated and quantitatively studied.

Excellent reviews of the flowing afterglow technique have been published by Graul and Squires in 1988 [5] and by Bohme in 2000 [6], and there have been several summaries of its many

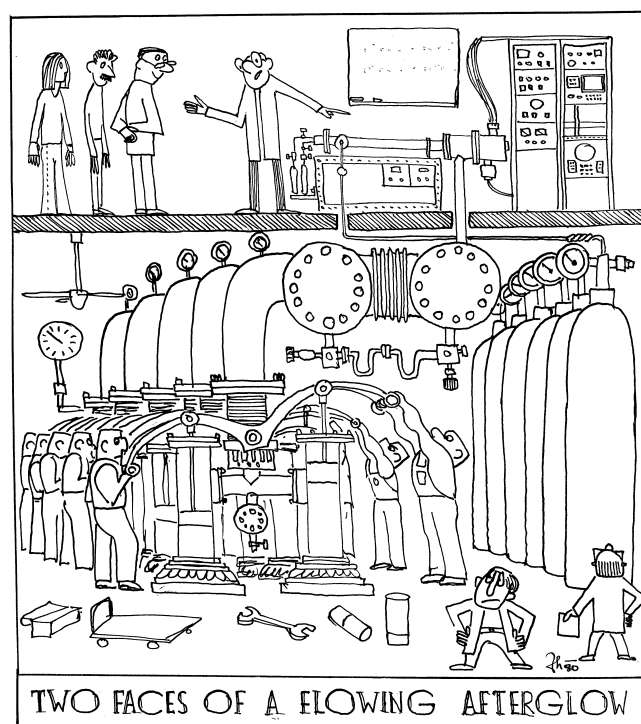


Fig. 3. Two faces of a flowing afterglow. (Drawing kindly provided by the artist, Zdenek Herman.)

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