SAMUEL PARSONS MULLIKEN: PIONEER IN ORGANIC QUALITATIVE ANALYSIS

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Introduction

Most chemistry majors in the decades from the 1910s through the 1970s remember the organic qualitative analysis laboratory—some fondly, some otherwise. Whatever the recollection, "organic qual" served and continues to serve many purposes, most notably the development of critical thinking and logical analysis skills. Systematic organic qualitative analysis as a means to teach organic chemistry was largely an American invention, begun in the late nineteenth century by Dr. Samuel Parsons Mulliken at the Massachusetts Institute of Technology (MIT) (1, 2). Mulliken spent most of his career researching, teaching, and writing books about organic qual at MIT. This paper details the pioneering role of Professor Mulliken in the development of systematic organic qualitative analysis and presents some related aspects of his academic life. An earlier publication in THE NUCLEUS, the official publication of the Northeastern Section of the American Chemical Society, although touching on the development of organic qual, was mainly devoted to Mulliken's personal life and professional career (3).

Early Life in Newburyport, Massachusetts

Sam Mulliken was born in the family home at 46 High Street in Newburyport on December 19, 1864. His early interest in chemistry grew from reading "Conversations on Chemistry" by Jane Marcet, the same book that both his father, Moses Mulliken, and his son, Robert (chemistry Nobel Prize, 1966), read (4, 5). After graduating from Newburyport High School in 1881, Sam worked for two years in a local apothecary shop. With the help of one of the first Wheelwright Scientific Fund scholarships (6), he entered MIT in the fall of 1883. Sam's long-time friend and fellow Newburyport native, Arthur Amos Noyes, also entered MIT that same fall. Like Mulliken, Noyes received a Wheelwright scholarship and studied chemistry. As youngsters, Noyes and Mulliken performed chemical experiments together at both their family homes, sometimes to the dismay of their parents (4).

Graduate School

After graduating in chemistry from MIT in 1887, Sam taught chemistry at the University of Cincinnati for one year as an Assistant in Chemistry. He, together with fellow MIT graduates Arthur A. Noyes ('86), Augustus H. Gill ('86), and Frederick F. Bullard ('87), then traveled to Germany to pursue graduate study. Although he originally intended to work in Adolf von Baeyer's lab in Munich, Sam eventually enrolled at the University of Leipzig to work under the direction of Johannes Wislicenus. Mulliken received his Dr. in chemistry in the summer of 1890 and returned to America (7, 8).

Sam spent the winter of 1890 conducting physical-chemical research at MIT. In spring 1891 he obtained a position as Fellow in Chemistry at the newly established Clark University in Worcester, Massachusetts (9). During the 1891-92 academic year he worked at Bryn Mawr College as Associate in Chemistry, then returned to Clark to work as both Instructor in Organic Chemistry and
Acting Head of the Chemistry Department from 1892-94. While at Clark he conducted and directed research on the electrolysis of organic compounds (10). Subsequently, he worked for a year as a Research Assistant in Oliver Wolcott Gibbs' private laboratory in Newport, Rhode Island. In the Fall of 1895 Sam accepted an appointment as Instructor in the Chemistry Department at MIT (11, 12). While at MIT he was promoted to Assistant Professor in 1905, Associate Professor in 1913, and Professor in 1926 (13).

Massachusetts Institute of Technology - The Early Years and Arthur A. Noyes

Arthur A. Noyes had been in the MIT chemistry department for five years when Mulliken returned as a faculty member in 1895. Noyes, though initially trained as an organic chemist, soon embraced physical chemistry while simultaneously developing a life-long interest in inorganic qualitative analysis. As early as 1892 Noyes published a set of notes for the inorganic qual class at MIT (14). He wrote these because the available texts were either too brief or too encyclopedic for the undergraduate laboratory (15). In the preface to the third edition of the notes, written in 1897, he stated (16):

...qualitative analysis is a satisfactory method of teaching a part of descriptive chemistry chiefly because it unites into a connected whole a great variety of isolated facts, and because it makes evident to the student a practical use of the information presented to him.

In further pursuance of this dual "descriptive chemistry" and "practical use" approach, Noyes and the newly appointed Sam Mulliken set out at once to revamp the organic laboratory (17). As a result of their work, the descriptions of the organic laboratory changed, reflecting the shift in pedagogical philosophy. In the 1896-97 MIT catalog the organic laboratory is described as including (18):

the methods of ultimate analysis, followed by exercises in the preparation of a variety of typical organic substances and in original research.

In the following year the catalog read (19):

......comprises practice in the methods of ultimate analysis, exercises in the preparation of a variety of typical organic substances, and a series of experiments illustrating the characteristic reactions of the different classes of substances and their identification and separation (emphasis added by author).

The "series of experiments" highlighted the descriptive chemistry of the organic functional groups and the "identification and separation" illustrated a practical use of this knowledge. Thus the emphasis on descriptive chemistry and practical use initiated in the inorganic qual course was applied to the organic laboratory course. The 1896-97 MIT Annual Report states (20):

.....the special course of laboratory experiments on the detection and separation of the various classes of organic compounds, inaugurated last year...has been considerably extended and improved by the publication of a textbook to accompany it. So far as is known, a course of this kind is not as yet presented by any other institution. The success which has attended its introduction here, is, therefore, worthy of special notice.

Organic qualitative analysis as a part of the chemistry curriculum was born

The exact date on which these changes came into effect is difficult to determine because the inclusion of events in official catalogs and reports often follows their actual implementation. However, the facts that the accompanying textbook was published in 1896 (21), and that the 1896-7 annual report contains a discussion of the altered course suggest that the change was made in the fall of 1896. The fact that a description of the revised laboratory program first appeared in the 1897-8 catalog is explained by the early publication date of the catalog. It is reasonable to conclude that Mulliken and Noyes began their collaboration on organic qual as soon as Mulliken arrived in the fall of 1895, if not before.

The First Textbook

Laboratory Experiments on the Class Reactions and Identification of Organic Substances, pub-
lished in 1896 by Noyes and Mulliken (21), was the first systematic treatment of organic qualitative analysis designed for the academic laboratory. In the preface to its 1915 third edition it is stated that this is a (22):

...supplement to the ordinary course of instruction in preparation work (and)... although the primary purpose of the experiments ... is to illustrate the characteristic reactions of organic compounds, their analytical significance is a feature of no slight importance ....

The descriptive and practical aspects of this work were distinctively different from the usual routine organic synthetic methods of the time. Notably, Ira Remsen commended the text, stating that some books drive one "to get into a rut, to work mechanically ... without any accompanying action of the mind" and some do not. He counted the Noyes and Mulliken text in the latter category and suggested that it "will be of service" (23).

This was Mulliken's first, brief foray into a succession of treatises spanning the next 26 years, in which he outlined the analysis and identification of pure organic compounds. His interest in organic compound identification eventually turned his entire professional activities toward this effort. He developed and taught courses in undergraduate and graduate organic qualitative analysis; his thesis students worked on applicable laboratory techniques; and he limited his writing and speaking activities to the organic qualitative analysis volumes he was researching and about to publish.

The Mulliken Scheme for the Identification of Pure Organic Compounds

In the late 1890s Mulliken's research efforts shifted completely to his organic qual work. His conference presentations and publications included papers on the detection of methyl alcohol alone (24), and in mixtures (25) and the detection of the nitro group (26). After about 1900 he appears to have abandoned publishing separate journal articles on analysis and class reactions, opting instead to publish them as part of a major work on systematic organic qualitative analysis.

In February of 1903, at a meeting of the Northeastern Section of the American Chemical Society, Mulliken outlined his organic qualitative analysis scheme in an address entitled "How May an Unknown Organic Compound Best be Identified?" He is quoted in the notes of the meeting as claiming that (27):

...any organic compound may be accurately identified in much less time than by determining its composition by combustion, etc.

In 1904, after eight years of painstakingly detailed laboratory work, Mulliken published A Method for the Identification of Pure Organic Compounds - Volume I (28). This volume contains a detailed description of a method for the systematic identification of organic compounds containing carbon and hydrogen or carbon, hydrogen, and oxygen. It also includes descriptions of about 2,300 pure organic compounds composed of these elements. The method is based largely on chemical reactions, although some tests for physical properties are included. Subsequent Mulliken "Methods" volumes followed: Volume III (29) in 1910 deals with commercial dyestuffs; Volume II (30) in 1916 contains a description of organic compounds containing nitrogen; and Volume IV (31) in 1922 is a compilation of organic compounds containing elements other than carbon, hydrogen, oxygen, and nitrogen. The classification scheme, later known as the "Mulliken Scheme," developed in these "Methods" books was the first comprehensive, systematic approach to identify organic compounds by chemical reactions and physical properties. The "Methods" books were renowned for their extensive compilations of properties.
of organic compounds, the thoroughness with which all the qualitative schemes were described and tested, and the care taken to describe precisely the results (32).

The Mulliken qualitative scheme is based on the use of chemical reactions and physical properties to categorize unknown organic compounds into orders, suborders, genera, and divisions. It provides additional identification tests to confirm a specific compound or species. Mulliken compared his qualitative analysis classification with Carolus Linnaeus’ classification scheme developed for living things. He said his scheme was (33):

"...designed to secure for the carbon compounds those advantages which have been already so long enjoyed in Botany and other branches of Natural History through the use of systematized descriptions of salient characteristics."

It is not surprising therefore, that Mulliken grouped organic compounds into orders, suborders, genera, divisions, and species.

In Mulliken’s organic qual scheme, organic compounds are grouped into orders based on their elemental composition, and into genera based on chemical reaction tests. The species or chemical substances within each genus are arranged by some readily determined physical constant such as boiling or melting point. The genera are subdivided into divisions that represent solids or liquids. The scheme begins with a series of ordinal tests applied in hierarchical fashion, to determine the order of the species. Volume I deals only with Order I—that is, C, H or C, H, O—compounds. Volume II deals with Order II compounds, containing C, H, N, O. Volume IV deals with Orders III, IV, V and VII compounds containing chlorine, bromine, iodine and sulfur, respectively, in addition to C, H, and O, and several of the “higher orders” which contain various combinations of additional elements. For example, Order L contains chlorine and nitrogen in addition to C, H, and O. Volume III, which deals with commercial dyes, was not an integral part of the Mulliken qualitative analysis scheme.

Once its order is established, a compound is then placed into a genus by conducting a series of prioritized tests in sequence. For instance, for an Order I compound, the nine generic tests distinguish among aldehydes, carbohydrates, acids, phenols, esters, anhydrides, ketones, alcohols, and hydrocarbons. After the order and genus are determined, the boiling or melting point of the species is compared with those of known species listed in the same order and genus contained in the extensive lists provided in the book. Finally, examination of physical properties and confirmation tests establish compound identity (34).

Prior to the publication of the Mulliken Scheme in 1904 the only method for identification of previously characterized organic compounds was by empirical formula determination from combustion analysis, a lengthy and sensitive process. Mulliken considered his scheme more useful to practicing chemists because it did not rely on combustion analysis, was accurately conducted in any organic laboratory, and consumed less time than available methods (35).

The subject matter of the theses written by his undergraduate students shows the evolution of Mulliken’s analysis scheme. Beginning in 1897, his students explored the usefulness of reagents such as sodium, sulfuric acid (36), and acetyl chloride (37) in classifying organic compounds. It would appear that, during this time, he and his students experimented in determining suitable reagents to distinguish among major groups, or what were later called orders and genera, of organic compounds. Later student research became somewhat more focused in dealing with identification of specific compounds or species within genera. For example, Rickards’ work in developing a method for the identification of the more important carbohydrates and glucosides (38) resulted in a complete scheme for the individual identification of many carbohydrates. This scheme provided much of the framework for the identification of Order I, Genus II compounds—the carbohydrates. Sam’s undergraduate students are acknowledged by name in the prefaces to Volumes I and II of the Methods series. The use of undergraduates in this research was essential because MIT awarded very few masters and no doctorates during the time Mulliken was actively pursuing the details of the scheme.

**Other Organic Qual Schemes**

Shortly after Mulliken’s pioneering publication appeared in 1904, others put forth their own organic qualitative analysis schemes. One of the most successful was that taught in 1920 by Oliver Kamm at the University of Illinois (39). He based his scheme on the solubility classification of organic compounds into seven groups, and subsequent identification by physical and chemical properties and derivative preparation. Kamm published his scheme in 1922 in a book entitled *Qualitative Organic Analysis—An Elementary Course in The Identification of Organic Compounds* (39). In the preface to the book he states that(40):
The chemist to whom most credit is due for the development of organic qualitative analysis is Professor S. P. Mulliken.

In the same preface he refers to Mulliken as "the pioneer in the field." Indeed, Mulliken was the pioneer in the field but it was Kamm's solubility approach that quickly emerged as the organic qual scheme used in colleges and universities around the country. In the preface to the second edition of his book, Kamm mentions over twenty organic chemistry teachers from around the country who used his first edition, and who provided suggestions for the second (41). On the contrary, Mulliken's "Methods" books, although frequently used as references (42), were rarely assigned as laboratory texts.

In 1935 Ralph Shriner and Reynold Fuson, both from the University of Illinois, published their text, *The Systematic Identification of Organic Compounds- A Laboratory Manual*, which was based on Kamm's original solubility scheme (43). Shriner and Fuson's seventh edition (with co-authors) is still used in some colleges today. However, the increased availability and usefulness of spectroscopic methods beginning in the late 1960's resulted in the end of the organic qual course, as it was known in the first half of the century.

In 1929 Mulliken invited his MIT chemistry department colleague, Ernest H. Huntress, to work with him in both revising the "Methods" books and condensing their analytical procedures into a manual suitable for use in the undergraduate laboratory. Huntress partially accomplished the first of these tasks by revising Mulliken's Volume I, which was published in 1941 (44). Huntress worked essentially alone in this effort because of Mulliken's death in 1934. Volumes II and III were never revised. Huntress did, however, update Volume IV during World War II because of the growth in the number of higher order compounds and the specific interest of the Chemical Warfare Service in Order III chlorine-containing compounds (45). This new volume, entitled *Organic Chlorine Compounds*, was published in 1948 (46). During the 1930s Huntress also produced and locally published a laboratory manual based on the "Mulliken-Huntress" scheme for use by MIT students (47). Although intended for MIT students, the Mulliken-Huntress lab manual was used by many other colleges (48). In the early 1950s Huntress passed on the rights to the scheme to Dr. Edward R. Atkinson, his former doctoral student (Ph.D. 1936) and Mulliken's former lab assistant in 1933 (45). Dr. Atkinson retains these rights to this day, although he has not revised or republished the scheme.

In the final analysis it appears that the reasons the Mulliken, later the Mulliken-Huntress organic qual scheme never gained wide popularity were many. The original "Methods" books were not intended for undergraduate laboratory instructional use, but rather for professional analysts and as reference works (49). Contemporary texts used in the undergraduate laboratory, for instance, Clarke's *Handbook of Organic Analysis*, were comprehensive, single volumes containing tables of only the most common organic compounds (50). By the time Huntress condensed the "Methods" texts into a practical, single volume manual of procedures, the Shriner and Fuson text was widely available. Further, the Huntress-Mulliken manual was published locally and primarily known by word of mouth (45, 51). It contains neither discussion of mixture separation nor student problems, unlike the Shriner and Fuson text, which was marketed nationally. Furthermore, the latter text relied more extensively on derivative preparation than on the extensive compilation of information about individual organic compounds found in the Mulliken-Huntress manual. For all these reasons, the popularity of the Shriner and Fuson text rose and that of Mulliken-Huntress faded. Later editions of the Shriner and Fuson text are in use today while the Mulliken "Methods" texts and the Mulliken-Huntress manual are rarely found.

**Dye Chemistry**

Mulliken had a life-long interest in dye chemistry and consulted in the dye industry. This interest likely developed because of the timely importance of the textile industry in his Newburyport home town, the applied
nature of chemistry taught at MIT, and the fact that many
MIT students were employed in the textile industries.
The nearby cities of Lowell and Lawrence were re-
nowned for their textile mills, and Lowell was home to
the Lowell Textile Institute and the famous textile dye
authority, Louis Olney. Sam developed and taught a
course in dye chemistry at MIT, and he regularly took
students on field trips to textile companies in Lawrence
as part of the course. His long-standing interest in dyes
is evidenced in “Methods” Volume III that deals with
the qualitative analysis of commercial dyestuffs.
Mulliken had no intention of writing a separate volume
on the identification of commercial dyestuffs (52) but
was apparently per-
sued that this venture
was of sufficient impor-
tance to put aside his
work on completing
Volume II. Indeed, Vol-
ume III appeared six
years before Volume II!
An explanation as to
why the dyestuffs vol-
ume was pursued and
completed prior to Vol-
ume II is open to specu-
lation. Mulliken may
have been pressured by
outside sources to help
the American textile in-
dustry in the identifica-
tion of commercial dye-
stuffs or it may have
been that Mulliken in-
tended to include the
dyestuffs as part of Vol-
ume II but determined
that they would be more effectively treated separately.
Potential arguments for both these scenarios are to be
found in Chapter One of Methods – Volume III.

The Later Years

During his 39 years of teaching at MIT, Mulliken taught
courses in undergraduate organic chemistry, qualitative
organic analysis, chemistry of dyes and dyestuffs, and
heterocyclic chemistry. Outside the classroom Sam was
active in the professional chemistry society Alpha Chi
Sigma, served on several MIT committees such as the
Committee on Determining Official MIT Colors, and
represented his graduating class of 1887 at Alumni Coun-
cil meetings. He also occasionally accepted administra-
tive responsibilities. One such position was as Head of
MIT’s Undergraduate Organic Chemistry Division from
1925 to 1934, when he directed the undergraduate in-
structional work (53,54). In 1933, Sam was asked to
pass judgment on an MIT undergraduate who sought a
waiver from the organic chemistry requirement. Reluc-
tant to grant such a waiver, believing that the require-
ment should be fulfilled, he met with the student and
eventually allowed him to take the course final exami-
nation. The student passed and Sam approved the waiver
(55). The student was Robert Burns Woodward, and no
one would deny that Mulliken’s decision in this case
was indeed warranted!

By the

Spring of 1934
Sam was old
and tired,
regularly fall-
ing asleep in
his Morris
chair in his of-

fice in Room
4-440 at MIT.
He last taught
during the
1933-34 ac-
demic year
and then took
his second
leave of ab-
sence from
MIT for the
fall of 1934.
During his
first leave in
the fall of 1918 he had worked for Chemical Warfare
Service. In the summer of 1934 he contracted rheumatic
fever and was hospitalized in Newburyport. He died at
home of a coronary thrombosis on October 24, 1934
and was buried at the Oak Hill Cemetery in
Newburyport. Many MIT chemistry department fac-
ulty attended the funeral. Ten MIT faculty served as
pallbearers: Frederick G. Keyes, Augustus H. Gill,
James F. Norris, Arthur A. Blanchard, Avery A.
Ashdown, Tenney L. Davis, Avery A. Morton, Ernest
H. Huntress, N. A. Milas, and Robert T. Armstrong
(56,57). Sam’s tombstone is engraved with his profes-
sional achievements, including his Dr. from Leipzig and
posts he held at MIT.

MIT Chemistry Department Faculty circa 1900 including
Ellen Swallow Richards
Upon his death in 1934, Mulliken’s professional belongings in Room 4-440 at MIT passed on to his faculty colleague and organic qualitative analysis collaborator Ernest H. Huntress. Over the next several years Huntress gradually disposed of the voluminous chemical samples Sam had stored there. Today, after renovations at MIT, no trace of Mulliken’s office and laboratory space remains. There is, however, a photograph, circa 1899-1900, of the MIT Chemistry Department in a lobby on the first floor of Building 4 honoring Ellen Swallow Richards. Samuel Parsons Mulliken is in the second row, third from the right, directly behind Mrs. Richards (58).

NOTE: A complete listing of the publications of Samuel Parsons Mulliken and a listing of his known students and their thesis titles are available from the author upon request.

REFERENCES AND NOTES

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27. M. Comey, in *Minutes of the Northeastern Section of the ACS, 1898-1908*, Meeting of February 27, 1903, 83-84. [Available from Dr. Myron Simon, archivist of the Northeastern Section, Regis College, Weston, MA]
33. Ref. 28, p iv.
34. Ref. 28, p 1-8.
35. Ref. 28, p iii-iv.
37. C. W. L. Petee, Use of Bromine, Ferric Chloride and Acetyl Chloride in Qualitative Analysis, B.S. Thesis, MIT, 1897.
41. Ref. 39, p v.
45. E. R. Atkinson, "Organic Qual – II," THE NUCLEUS, 1979, 57(5), 6-8. See also Dr. Atkinson’s other articles on this topic in THE NUCLEUS, 1979, 57(4) and 57(6).
52. Ref. 29, p iii.
57. Ref. 56. October 29, 1934, 1.

ABOUT THE AUTHOR

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BSHS IVAN SLADE PRIZE

The British Society for the History of Science is pleased to announce the inauguration of a new prize generously donated by one of its members, Dr. Ivan Slade. The competition will take place biennially, and the prize of GBP 300 is offered for an essay (published or unpublished) that makes a critical contribution to the history of science. Examples would be scholarly work that critically engages a prevalent interpretation of a historical episode, scientific innovation, or scientific controversy.

The prize will be awarded for the first time in 1999. Submissions are now invited. There is no age limit, and entry is not limited to members of BSHS or UK citizens. Entries should be in English and should have been published or written in the two years prior to the closing date. They should not exceed 10,000 words in length and should be accompanied by an abstract of 500 words. Three copies of the essay and abstract should be sent to the BSHS Secretary, Dr. Jeff Hughes, CHSTM, Maths Tower, University of Manchester, Manchester. M13 9PL, to arrive by October 31, 1999.