

Remembering Qualitative Analysis

The 175th Anniversary of Fresenius' Textbook

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The teaching of a course in systematic inorganic qualitative analysis was a staple of the undergraduate chemistry laboratory for nearly 140 years. Though such courses began to gradually disappear from the curriculum – at least in the United States – starting in the 1970s, 2016 was the 175th anniversary of the publication of what is perhaps the single most influential textbook on the subject – Carl Remigius Fresenius' *Anleitung zur qualitativen chemischen Analyse* – and it seems appropriate to celebrate this event with a review of the history of this rapidly disappearing laboratory technique.

Precipitants, Reagents and Test Solutions

It has long been known that, just as so-called “dry” or blowpipe analysis evolved from traditional metallurgical assaying techniques, so “wet” or solution analysis, in both its qualitative and quantitative forms, evolved from a traditional interest in the evaluation of the medicinal properties of mineral waters (1, 2). As shown by Debus, water analysis prior to the 17th century relied almost exclusively on distillation and such physical properties as the color, taste, odor, and crystalline form of the resulting distillation residue (3). Only in the 17th century does one see an increasing realization that the analytical detection of a metal did not always require its reduction and isolation, as in a standard fire assay, but could also be done indirectly in aqueous solution through the use of characteristic color and precipitation reactions. Examples, such as the use of vegetable dyes to detect acids, copper compounds to detect ammonia, and nut gall to detect iron, can be found in the writings of several 17th-century chemists, including Libavius, Hoffmann, Glauber, Tachenius, and especially Robert Boyle (4).

However, it was not until the last quarter of the 18th century that an attempt was made by the Swedish chemist, Torbern Bergman (figure 1), to systematically collect and evaluate these tests in his 1778 essay “De analysi aquarum” (5). In this essay Bergman reviewed in great detail the nature and preparation of 23 different



Figure 1. Torbern Bergman (1735-1784).

aqueous test solutions commonly used in water analysis. Bergman referred to these solutions as “precipitants,” but in an editorial footnote to the 1784 English translation of his essay, the British chemist, Edmund Cullen, referred to them instead as “reagents,” a term which he attributed, in turn, to the French chemist Guyton de Morveau, though, more recently, de Menten has suggested even earlier French antecedents (6, 7).

The etymological reasoning behind this term seems to have been that the unknown species in the analysis functioned as the active “agent” and the test solution employed to detect it as the passive “reagent” in the ensuing chemical interaction between the two. Likewise, whereas the unknown agent “acted” upon the reagent, the reagent itself merely “reacted” to this action. In other words, reaction was to action as reagent was to agent, where agent and action described the causative factors and reagent and reaction described the responding factors. Obviously both the terms chemical reaction and chemical reactant also



Figure 2. Heinrich Rose (1795-1864).

evolved from this same usage.

To confuse matters further, for the first three decades or so of the 19th century British chemists frequently referred to reagents as “test solutions” or “tests” for short, as may be seen from the chests or cabinets of “chemical tests” offered for sale by such chemists as Accum, Henry, and Griffin during this period (8). Thus, for example, Accum, in his 1816 *Practical Essay on Chemical Re-agents or Tests*, used the two words interchangeably and defined them as those (9):

... substances which, when applied to other bodies, the nature or composition of which are unknown, quickly act upon them, and produce such changes as are sufficiently striking to the senses, and from which the qual-

ity or nature of the unknown body may be inferred ... Most of the tests employed in the processes of chemistry indicate the component parts of bodies by occasioning either a precipitate, a sensible cloudiness, a change in color, an effervescence, or such other alterations of properties as experience has proved denote the presence or absence of certain bodies.

Though possibly a bit too wordy for the modern reader, most would nevertheless agree that this definition is as valid today as it was in 1816. However, while we still use the word test to describe either the act of analysis or the procedure used, we no longer use it as a synonym for reagent.

Group Reagents

The above authors presented the various reagents they discussed as specific tests for individual metals and acid radicals, but gave no advice on how to systematically combine them into a single sequential analytical scheme. The key to this development was actually the introduction of “group” reagents, rather than specific reagents, which could precipitate entire clusters of related metals. Application of these in the proper order allowed an analyst to separate the components of a complex mixture into ever smaller groups of related metals before applying the final confirmatory tests for each individual.

The first significant step in this direction was taken by the German chemist, Heinrich Rose (figure 2), in his 1829 monograph *Handbuch der analytischen Chemie* (10, 11). Both the group reagents employed by Rose and the various metals in each group are summarized in Table 1, where they are compared with those used by Sorum in the 1960 edition of his qual manual (12, 76). As may be seen, save for the presence of Au, Pt, and Sr in Rose’s scheme, the two are essentially identical, though there are, of course, many minor dif-

Table 1. A comparison of the qual groups and reagents used by Rose and Fresenius with those used by Sorum.

Group Reagent	Rose & Fresenius (1829, 1841)	Sorum (1960)
HCl	Ag, Hg, Pb	Ag, Hg, Pb
H ₂ S	Au, Pt, (Hg), (Pb), Bi, Cu, Cd, As, Sb, Sn	(Hg), (Pb), Bi, Cu, Cd, As, Sb, Sn
(NH ₄) ₂ S	Fe, Al, Cr, Co, Ni, Mn, Zn	Fe, Al, Cr, Co, Ni, Mn, Zn
(NH ₄) ₂ (CO ₃)	Sr, Ba, Ca	Ba, Ca
None	Mg, Na, K, NH ₄	Mg, Na, K, NH ₄

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ferences in how these groups were subsequently further separated and in some of the final confirmatory tests. The point, however, is that Rose established the basic outlines of systematic qualitative inorganic analysis as it would be practiced for the next 185 years. In making this table I have avoided using such labels as Group I, Group II, etc. for the simple reason that Rose arbitrarily chose to number his groups of metals in an order opposite that of their order of separation, such that the alkali metals were in Group I rather than Group V, the alkaline earth metals were in Group II rather than Group IV, etc. – a practice that was followed by subsequent qual manuals for much of the 19th century.

As suggested by his use of the term *Handbuch*, Rose intended his monograph to be a reference work for practicing analytical chemists and not a textbook for beginning students. It was over 600 pages long and his pedantic organization of the contents was, in the words of Szabadvary, “very dull” (4). Thus it was that the task of extracting the essence of Rose’s insights and presenting them in a simplified format suitable for undergraduate instruction fell instead to a young German chemist by the name of Carl Remigius Fresenius (figure 3).

Fresenius first made his simplified abstract of Rose while still a student at the University of Bonn and in 1841, upon his transfer to Liebig’s laboratory at Giessen, used it to teach an introductory course in qualitative inorganic analysis (13). The first edition of 1841 was quickly succeeded by a second in 1842, which carried a preface and endorsement by Liebig, by a third in 1844, and by a fourth in 1846, by which time Fresenius had transferred to Wiesbaden, where he eventually founded the *Zeitschrift für analytische Chemie* in 1862 and a family dynasty of analytical chemists that would include two of his sons and a grandson as well. By the time of his death in 1897 his textbook had passed through 16 editions and in 1919 his son, Theodor Wilhelm Fresenius, published yet a 17th edition (14). However, this was over 950 pages thick and had thus, rather ironically, degenerated into a reference work, not unlike the handbook of Rose that it had originally been intended to supplement 80 years earlier. Finally, in 1942, or slightly over a century after the appearance of the first edition, Fresenius’ grandson, Remigius Fresenius, coauthored a highly condensed (207 pages) introductory manual under a new title which recaptured the spirit and intent of the first edition (15).

Within three years of its initial publication, the Fresenius manual was translated into English, French, Italian, Dutch, Spanish, Hungarian, Chinese, and eventually Russian. In this manner it rapidly spread the



Figure 3. Carl Remigius Fresenius (1818-1897).

“Giessen method” of teaching introductory qualitative inorganic analysis throughout the civilized world. By the end of the 19th century essentially every university in the United States, Great Britain, and Continental Europe had its own in-house qualitative analysis manual whose contents were ultimately traceable to Fresenius, and by mid 20th century the number of books published on this subject probably numbered in the hundreds. Despite the many subsequent attempts, discussed below, to alter the original qual scheme outlined by Rose and Fresenius, it would prove to be remarkably resilient, as may be seen from the comparison given in Table 1.

There is, however, a curious puzzle connected with the Giessen origins of qualitative analysis. In 1845 a second manual of qualitative analysis, also containing a preface and endorsement by Liebig, was published by Heinrich Will under the title *Anleitung zur chemischen Analyse zum Gebrauche im chemischen Laboratorium zu Giessen* and which, as may be seen, explicitly stated in its title that it was based on the official course used at Giessen (16). Will had been a student at Giessen since 1837 and a Privatdozent since 1839. Apparently he took over undergraduate instruction in qualitative analysis after Fresenius’ departure in 1845 and felt compelled to issue his own laboratory manual. This was in many ways a terse condensation of the manual by Fresenius, and it would be of some interest to know what the original author thought of this turn of events. Will would remain at Giessen his entire career and would succeed Liebig as Professor of Chemistry there after the latter’s departure for Munich

in 1852. Though Will's textbook would also undergo several editions and translations, it was never as influential as the volume by Fresenius.

Mention should also be made of yet a third condensation of Rose's analytical scheme for the beginning student. This was published in 1849 under the title of a *Practical Introduction to H. Rose's Treatise on Chemical Analysis*, and was the work of the British chemist, A. Normandy, who had first translated Rose's *Handbuch* into English several years earlier (17). Rather curiously, in his introduction, Normandy made no mention of the books by either Fresenius or Will, though both had by this time been available for some years in English translation. Perhaps, because of this lack of awareness, his small manual appears to have had little or no impact on the subsequent development of qualitative analysis.

The first thing that strikes the modern reader of the pioneering books by Fresenius and Will, aside from the curious inversion in the numbering of the analytical groups commented on earlier, is that the laboratory instructions, especially in Will's manual, are not very specific. Unlike modern qual manuals, in which the student is told at each stage how many drops of reagent A or B to use, how much water to use when washing a precipitate, how many times to repeat the wash, or when to centrifuge, etc., nothing is said in these early manuals about what quantity or concentration of reagent to use or even about what equipment to use. Also conspicuously absent from both books are the flow charts used in later qual manuals to outline the overall separation scheme, though the manual by Will does contain several foldout tables designed to serve the same purpose.

What the two manuals have in common, however, is the so-called "100 Bottle Challenge." In other words, each student was required to demonstrate his mastery of the qual scheme by successfully analyzing 100 unknowns of ever increasing complexity (16):

The contents of the bottles become more and more complex as one advances from 1 to 100. In the first ten solutions one seeks only an acid [i.e. anion]; in the second ten, perhaps only a base [i.e. cation]. The next twenty are solids, and both an acid and a base are to be sought in each bottle. Then occur bottles, each containing several bases, then others, each containing several acids; and thus increasing, till the last ten of the hundred bottles may be found to contain from ten to twenty ingredients.

It is very difficult to imagine modern-day freshmen surviving such a challenge.

Theory

The above quote also calls attention to yet a third feature of these early manuals which will strike the modern reader as unfamiliar – namely their pervasive use of dualistic formulas and terminology. Based on the work of Lavoisier and Berzelius, the dualistic theory viewed ternary and other higher-order compounds as additive adducts of a basic metallic oxide and an acidic nonmetallic oxide. Thus calcium sulfate was thought of as an adduct of basic calcium oxide and acidic sulfur trioxide or as $\text{CaO}\cdot\text{SO}_3$. In keeping with this, basic solutions of calcium hydroxide were viewed as aqueous solutions of CaO , in which CaO , rather than hydroxide, was thought to be the source of the basic properties, and sulfuric acid as an aqueous solution of SO_3 , in which SO_3 , rather than hydrogen, was thought to be the source of the acidic properties – whence the use of the terms acid and base when referring to the nonmetallic and metallic components of salts.

In keeping with these usages, the manuals of both Fresenius and Will were organized around an analysis for the presence of various metallic oxides rather than for either simple metals or cations. In the companion field of quantitative analysis this practice of reporting the composition of a ternary salt in terms of its so-called component oxides, rather than its component elements, persisted well into the 1970s. Yet further complications arose from the fact that many atomic weight values used at the time were incorrect and thus the formulas of many compounds as well. For example, water was written as HO instead of as H_2O and sodium carbonate as $\text{NaO}\cdot\text{CO}_2$ rather than as $\text{Na}_2\text{O}\cdot\text{CO}_2$, etc.

These problems were only corrected in the 1860s as a result of Cannizzaro's famous pamphlet of 1858. This led not only to our current system of atomic weights, but also to our current method of writing the chemical formulas of salts, so that calcium sulfate now appeared as $\text{Ca}(\text{SO}_4)$ rather than as $\text{CaO}\cdot\text{SO}_3$. Yet, if one is to judge from various American editions of Fresenius, these changes did not begin to impact on his qual manual until the 1870s. Thus the 1871 reprint of the 1864 edition included an introductory essay by the book's translator, Samuel Johnson of Yale University, entitled "Chemical Notation and Nomenclature: Old and New," but made no attempt to revise the older dualistic formulas within the body of the text itself (18). It was only with the edition of 1875 that this revision was finally made and the subtitle "New System" added to both the spine and title page (19).

The theoretical revisions required by the so-called "New System" of the 1860s were minor compared with the upheaval caused in the 1890s by the introduction of



Figure 4. Wilhelm Ostwald (1853-1932).

the theories of ionic dissociation and chemical equilibrium. These two theories were the main bulwark in the 1880s of the new and rising discipline of physical chemistry championed by Arrhenius, van't Hoff, and especially by the Latvian/German chemist, Wilhelm Ostwald (figure 4). Indeed, it was Ostwald who first drew attention to their significance for the traditional practice of qualitative analysis in his classic 1894 monograph *Die wissenschaftlichen Grundlagen der analytischen Chemie* (20).

Ostwald's little book had an immediate impact. By the first decade of the 20th century numerous manuals of qualitative analysis were incorporating brief introductory sections on the theory of ionic dissociation and the laws of equilibrium and mass action, and were treating the subject as a procedure for the detection of ions rather than elements or oxides – though rather curiously the use of net ionic equations appears to have been uncommon before the 1930s. Some typical American examples include the manuals by Prescott and Sullivan (1902), Morgan (1906), Prescott and Johnson (1907), Medicus (1908), and Hinds (1910). In 1909 the French chemist, M. G. Chesneau, published an advanced monograph on the theory of chemical analysis emphasizing the same physico-chemical principles as Ostwald but from a uniquely French perspective (21), and in 1911 Julius Stieglitz of the University of Chicago published a two-volume

introductory treatise on qualitative analysis, the first volume of which was devoted exclusively to theory (22) – a pattern that would later be imitated by others as well (23). With these events qualitative analysis acquired a theoretical structure that it has retained even to this day and one, as we will see below, that would have profound pedagogical consequences.

Spot Reactions

In the early decades of the 20th century a school of analytical chemistry arose in Austria dedicated to the scaling down of conventional analytical techniques. The first and most famous of its practitioners was the Austrian chemist, Fritz Pregl, who was awarded a Nobel Prize in 1923 for his development of organic micro-combustion analysis (24). Starting around 1918 a second Austrian chemist by the name of Fritz Feigl (figure 5) decided to do for qualitative analysis what Pregl had done for combustion analysis, the results of which were first summarized in his 1931 monograph *Qualitative Analyse mit Hilfe von Tüpfelreaktionen* (25).

Usually translated as either “spot” or “drop” reactions, Feigl replaced the conventional macro beaker and test-tube level precipitation and color reactions used in qual with semi-micro and/or micro equivalents that employed only a drop of both the unknown and the reagent, and which were usually performed either on a piece of filter paper or in a porcelain drop plate. In order to attain as much specificity as possible for a

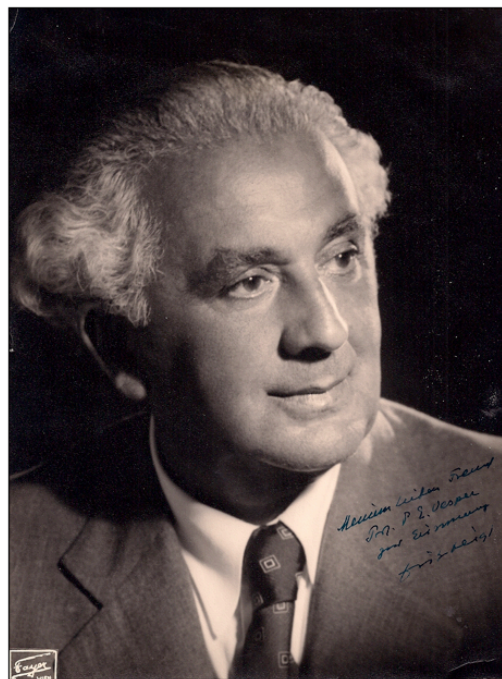


Figure 5. Fritz Feigl (1891-1971).

given test, Feigl also made heavy use of specially designed organic reagents, masking agents to eliminate interfering ions, and catalytic effects to amplify certain reactions. His monograph was soon translated and would go through numerous editions, the most recent of which appeared in 1983 (26). Indeed, so great were the advances in this area that each new edition would lead to a virtual doubling of the book's size.

It is important to realize that Feigl's work was directed at the practicing analytical chemist and not at the teacher of undergraduate courses in qualitative analysis. Though spot tests soon proved to be a highly effective way of testing for known ions under well defined conditions, such as the detection of trace contaminants, their open-ended application to the analysis of complex mixtures of unknowns was more problematic. While the ultimate goal was to develop spot tests that were each specific for one and only one ion, and thus eliminate the necessity for separations, practice always fell short of this ideal. Consequently, in each edition Feigl would summarize various imperfect proposals for a proper sequential application of the tests and would also organize his discussion of the various spot tests for individual metallic cations using the standard groups of the conventional qual scheme.

This strongly implied that one way to utilize the various spot tests was to first separate the ions in a

complex mixture using the conventional qual scheme and reserve use of spot reactions for the final confirmatory tests. In fact in 1933 the Dutch analytical chemist, C. J. van Nieuwenburg, published an undergraduate lab manual based on this exact premise (27), though it was not until 1940 that C. W. Davis finally brought van Nieuwenburg's proposals to the attention of American chemistry teachers (28).

Scaling Down

As events turned out, however, few American chemistry teachers would adopt van Nieuwenburg's suggestions concerning the use of spot reactions for confirmatory tests in the undergraduate qual course, largely for the reasons that will be outlined below in the section on pedagogy. However, they would adopt yet another of his suggestions – namely that the entire conventional separation scheme be scaled down to the semi-micro level. Throughout the 19th century and the first four decades of the 20th century, macro filtration was the standard way to separate precipitates and every qual manual contained illustrations of filter stands, and instructions for the use of both a wash bottle and the proper way to fold filter paper (figure 6). Van Nieuwenburg's suggestion, made almost as a passing comment and with virtually no detail, was that separations at

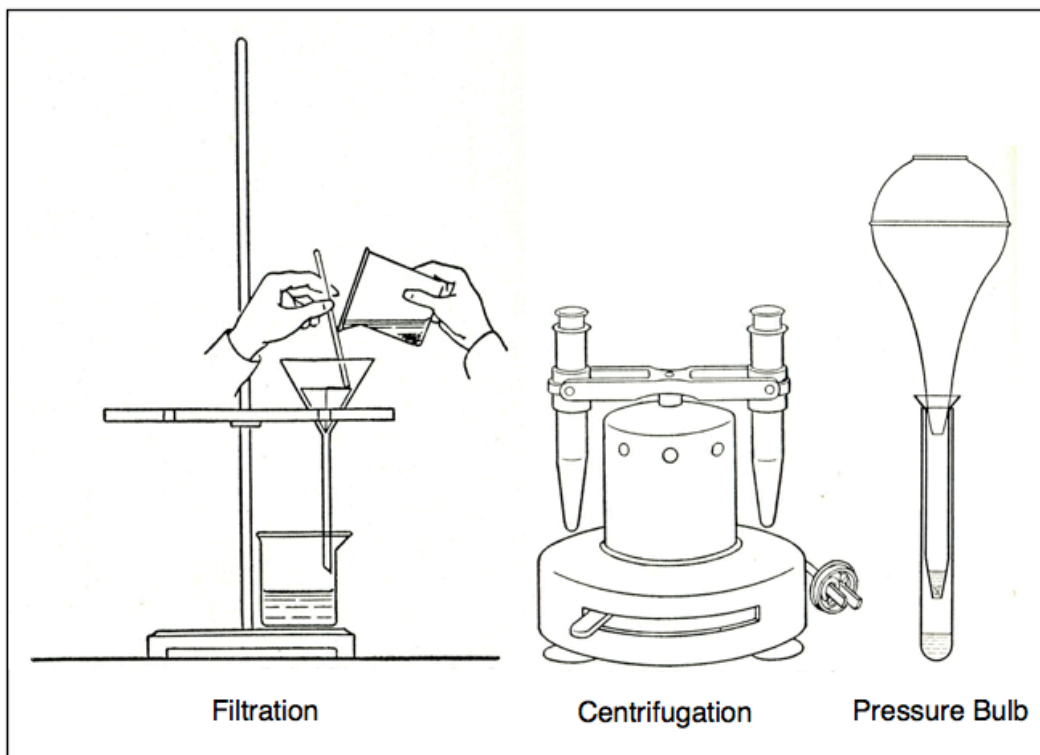


Figure 6. The evolution of separation techniques in qualitative analysis.

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the semi-micro level could be carried out using a centrifuge rather than filtration.

This same suggestion was independently made about the same time by C. J. Engelder and W. J. Schiller of the University of Pittsburgh (29). Inspired, like van Niewenburg, by the work of Feigl, in 1936 these authors, in collaboration with T. H. Dunkelberger, published a detailed laboratory manual in which the term “semi-micro” was, for the first time, directly incorporated into the title and which not only used the centrifuge for all separations but also performed most of the precipitations and confirmatory tests in small centrifuge tubes rather than in conventional beakers or test tubes (30). If for no other reason than the economic savings that resulted from scaling down the conventional scheme, the proposals of these three authors quickly spread to other schools. Articles praising the semi-micro approach soon began appearing in the *Journal of Chemical Education* (31-33) and, with the publication of the second edition of their textbook in 1940, these authors were able to proudly proclaim that (30):

The first edition of this book, which introduced the semi-micro technique into hundreds of institutional laboratories and, to a considerable degree, revolution-

ized the laboratory instruction in qualitative analysis, has more than fulfilled the authors' hopes and expectations.

By the late 1940s and early 1950s the older macro approach to qualitative analysis, at least in the United States, had been almost totally displaced by the newer semi-micro approach. Not only were newer manuals based on this approach, but also the most recent revisions of older macro manuals. Thus the textbook by Curtman, which first appeared as a macro manual in 1916, would switch to the semi-micro approach in 1942 (34), and that of Sorum, which evolved from a macro manual first published in 1911, would switch in 1949 (76).

The introduction of the semi-micro approach also spelled the eventual demise of the glass-stoppered reagent bottle. These bottles, with their bevelled and frosted glass labels, had been a standard feature, in one form or another, of the chemical laboratory for nearly 150 years (figure 7), but were now being rapidly replaced by small dropper bottles (figure 8). Once lining the shelves of undergraduate laboratories by the hundreds, glass-stoppered reagent bottles are now a rarity in most chemical laboratories and are no longer offered for sale by some laboratory supply houses.

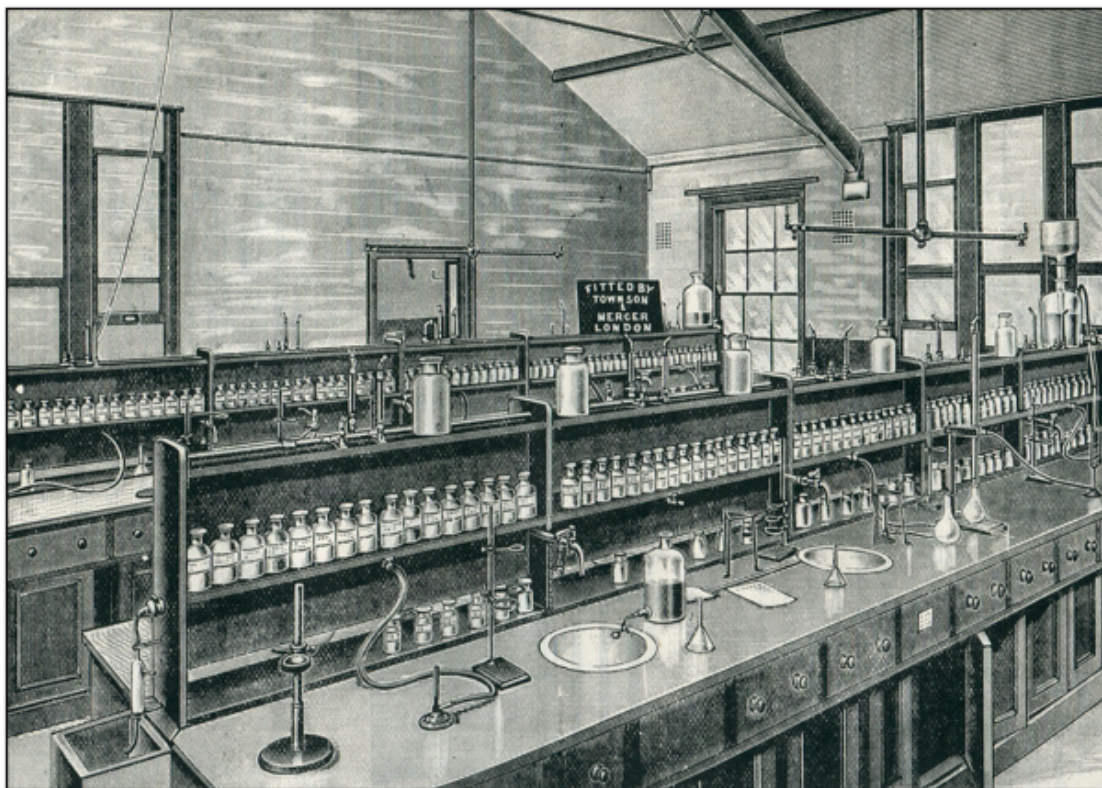


Figure 7. A typical, circa 1901, undergraduate laboratory showing the arrays of glass-stoppered reagent bottles.

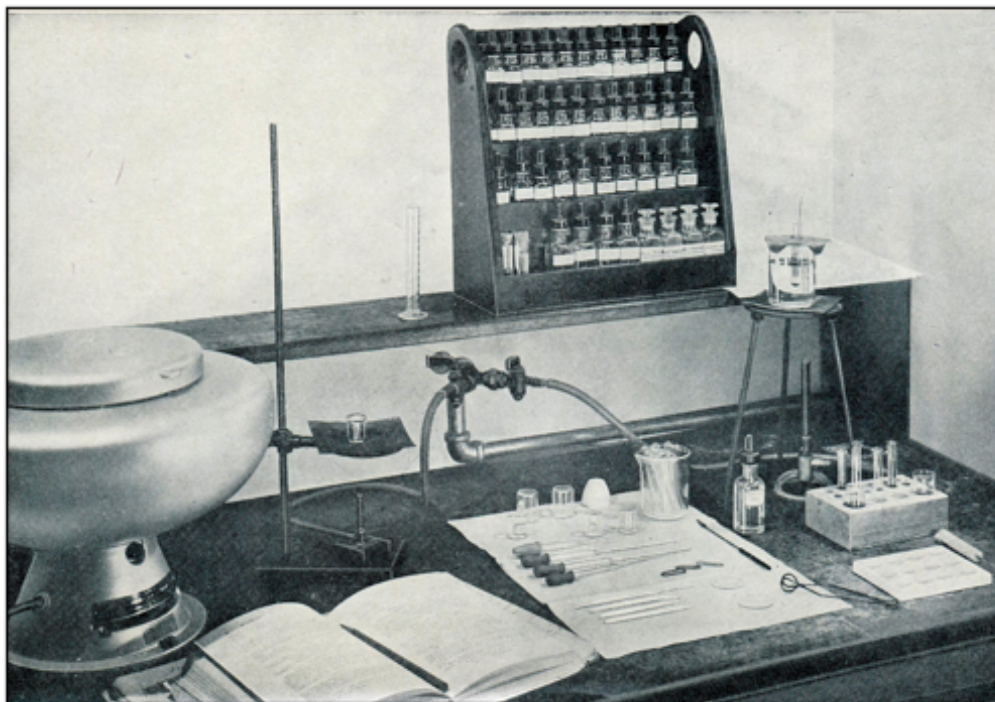


Figure 8. The apparatus and reagents needed for a course in semi-micro qualitative analysis, c. 1942. Note the replacement of most of the glass-stoppered reagent bottles by the rack of dropper bottles

Yet a third separation technique, also associated with the rise of semi-micro qual courses, was introduced in the 1940s by H. H. Barber of the University of Minnesota. Known as the “pressure bulb” method, it made use of a small centrifuge tube with a hole in the tip and a flared lip that allowed it to rest inside the top of a conventional test tube. A small plug of cotton was placed in the bottom of this tube and the liquid to be filtered was added and rapidly forced through the cotton plug using the air pressure from a small rubber bulb (figure 6). The pressure bulb method made the semi-micro approach even more economical by dispensing with costly centrifuges which often had short life-spans due to a combination of corrosive acids and sloppy undergraduate laboratory technique. This clever procedure and several others like it were described in great detail by Barber in his 1942 laboratory manual, but it is not known whether they were ever adopted beyond the confines of the University of Minnesota, where they originated (35).

Finally, mention should be made of yet a fourth separation method, known as the “ring furnace technique,” developed by the Austrian chemist, Herbert Weisz, in the late 1950s (36). However, this was specifically designed for micro-separations in conjunction with Feigl’s spot methods and was never, to the best of my knowledge, adapted for use in an undergraduate qual course.

Organic Reagents

As already noted, one of the characteristic features of Feigl’s spot analysis technique was the heavy use of specially designed organic reagents to improve the specificity of the various tests. Organic reagents had in fact been used since the beginnings of systematic qualitative analysis, but quite sparingly. Thus oxalate was used by both Rose and Fresenius to precipitate calcium. However, it wasn’t until 1905 that dimethylglyoxime was suggested by Tschugaeff as a confirmatory test for nickel (37), not until 1925 that aluminon was suggested as a specific reagent for aluminum (38), and not until 1977 that Sorum and Lagowski were willing to introduce the use of diphenylthiocarbazone as a confirmatory test for zinc in their well-known qual manual (77).

Meanwhile the design and use of organic reagents, not only in the field of spot analysis, but also in the fields of colorimetric and volumetric analysis (recall the impact of EDTA) had become so pervasive that in 1941 Yoe and Sarver could devote a 339-page monograph to the subject in which the analytical uses of more than 600 organic reagents were reviewed (39). Yet, despite the efforts of White three years earlier to convince chemical educators that organic reagents could be rationalized as logical extensions of more traditional inorganic reagents (40), the chemical educa-

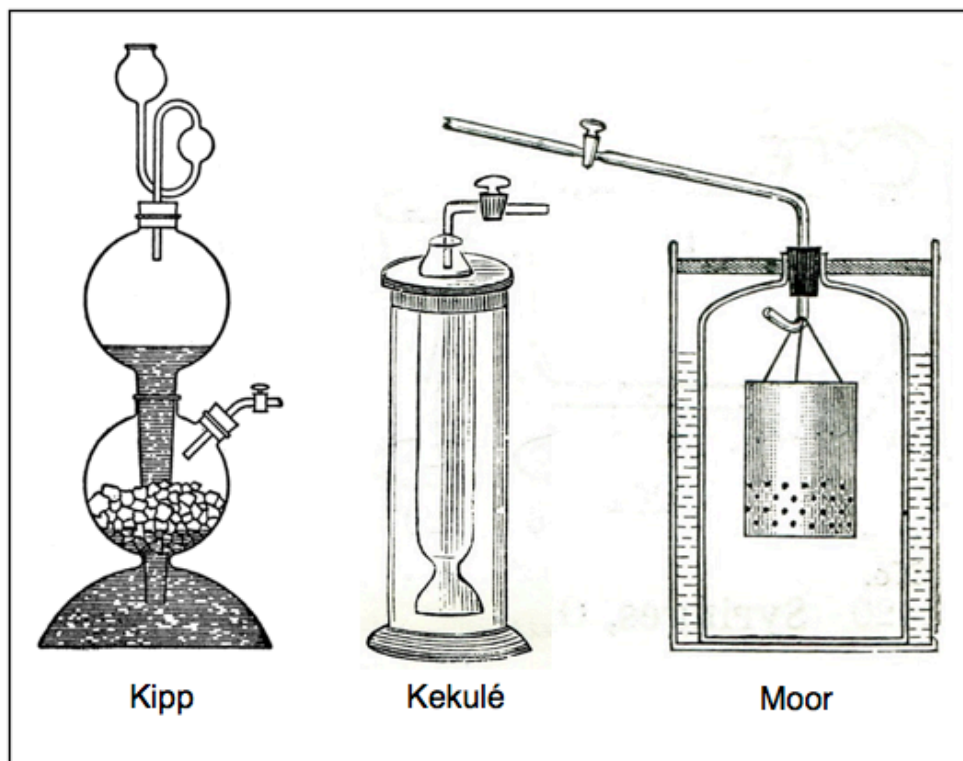


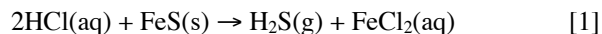
Figure 9. A small sample of the many hydrostatic HCl/FeS hydrogen sulfide generators proposed in the chemical literature.

tion community remained largely unconvinced and clung instead, with few changes, to the chemistry of the traditional qual scheme first introduced by Rose and Fresenius a century earlier.

The Hydrogen Sulfide Problem

The single most persistent problem to dog the teaching of qualitative analysis throughout its 175 years of existence was the problem of hydrogen sulfide, whether it be the question of the best method of generating and storing it in the laboratory, or – given its obnoxious odor and significant toxicity – the question of whether it should be dispensed with altogether.

For the first century or so this gas was usually generated using the reaction between aqueous hydrochloric acid and solid iron sulfide:



Though, like all gas-generating reactions involving solid and liquid reactants, this reaction could be carried out in a simple gas-generating bottle, this did not allow for stopping and starting the flow of gas as required. Consequently a variety of more elaborate gas generating devices were developed for this purpose, most of

which made use of either hydrostatics or gravity to provide the desired control (41).

The most famous of the hydrostatic or gasometer devices was the gas generator introduced by the Dutch apothecary and instrument maker Petrus J. Kipp in 1844. This consisted of three bulbs or sections (figure 9). The top most section was removable and served as a funnel and reservoir for the HCl(aq). The middle and bottom bulbs were a single unit and were joined by means of a narrow contraction or neck. The middle section also had an opening for an exit tube and stopcock and the bottom section an opening with a glass stopper, whereas the top section had a long stem that could be joined to the top of the middle section by means of a ground-glass joint and which passed through this section into the lower most section. The thickness of this stem was just sufficient to barely clear, but not seal, the contraction between the middle and lower sections.

With the bulbs in place, the stopcock was removed from the middle section and chunks of FeS(s) added through the opening until this section was about a quarter full. Because of the partial blockage of the opening between the middle and lower sections by the reservoir stem, these solid chunks could not fall into the bottom section. The stopcock was then reattached

and placed in the closed position, followed by addition of sufficient $\text{HCl}(\text{aq})$ to the top reservoir to fill the bottom bulb and, via the narrow neck, to cover the $\text{FeS}(\text{s})$ in the middle bulb. As the ensuing reaction generated $\text{H}_2\text{S}(\text{g})$, the increasing gas pressure in the middle bulb would force the $\text{HCl}(\text{aq})$ out of this bulb back into the lower bulb and up the stem of the reservoir, and thus terminate gas production. When the stopcock was opened to use the gas, the decreasing gas pressure in the middle bulb, in conjunction with the hydrostatic pressure in the reservoir, would force $\text{HCl}(\text{aq})$ back up into the middle bulb and thus once again allow generation of $\text{H}_2\text{S}(\text{g})$. The net result was a replenishable supply of $\text{H}_2\text{S}(\text{g})$ under moderate pressure that could be turned on and off at will.

By the second half of the century, laboratory supply houses were offering Kipp generators ranging in size from 250 mL to 4 L and literally dozens of variations were being proposed in the literature, some of which are shown in figure 9. Despite their great variation in shape and size, all of these generators worked on the same hydrostatic principle as Kipp's original device.

The most famous of the gravitational devices was the simple gas generator proposed by the German chemist Lambert von Babo. This consisted of two glass bulbs with openings connected by means of a curved glass tube and mounted in a stand that allowed them to be rocked back and forth (figure 10). The $\text{HCl}(\text{aq})$ was placed in one bulb and the $\text{FeS}(\text{s})$ in the other and the latter connected via its opening to a tube and stopcock. When the $\text{FeS}(\text{s})$ bulb was in the down position, the $\text{HCl}(\text{aq})$ would flow into the $\text{FeS}(\text{s})$ bulb and generate $\text{H}_2\text{S}(\text{g})$. When the $\text{HCl}(\text{aq})$ bulb was in the down position, the acid was no longer in contact with the $\text{FeS}(\text{s})$ and $\text{H}_2\text{S}(\text{g})$ generation would stop. Once again, many variations of this device were proposed, some of which are shown in figure 10. The only downside of these devices was, if the $\text{FeS}(\text{s})$ chunks became too small, they could be flushed into the $\text{HCl}(\text{aq})$ reservoir, with the result that lowering it would no longer terminate $\text{H}_2\text{S}(\text{g})$ generation.

By the beginning of the 20th century, laboratory classes in qualitative analysis at many universities had become so large that several schools actually piped $\text{H}_2\text{S}(\text{g})$, produced in large centralized cast-iron gaso-

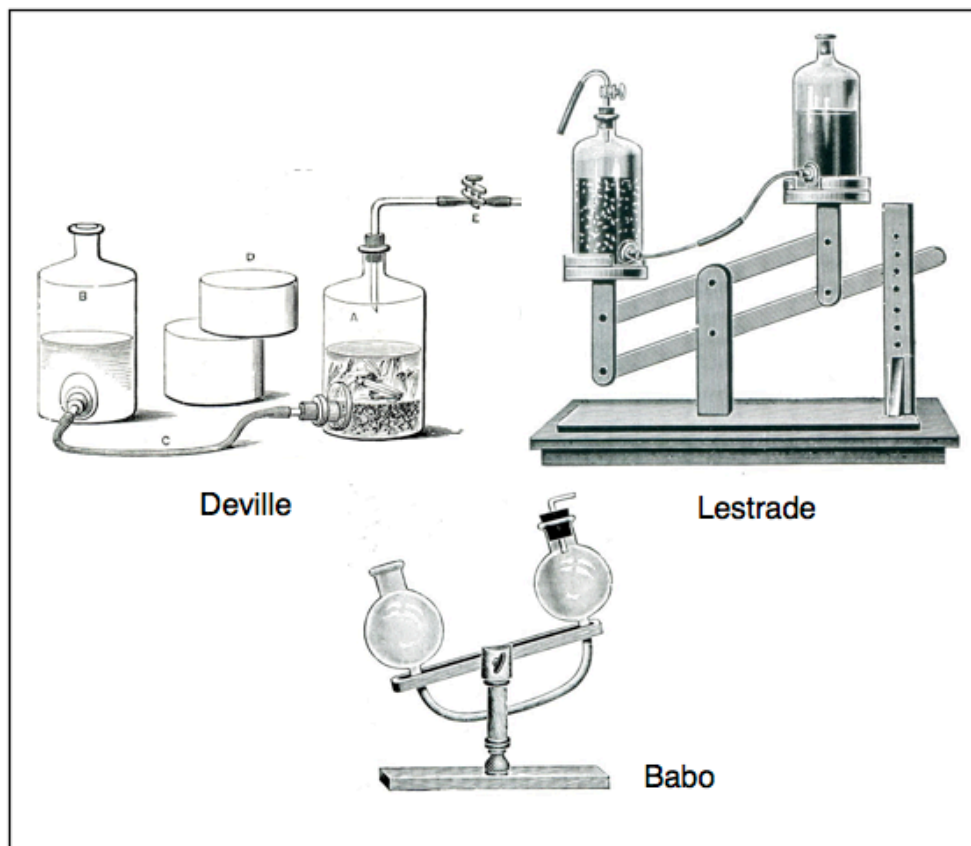


Figure 10. A small sample of the many gravitational HCl/FeS hydrogen sulfide generators proposed in the chemical literature.

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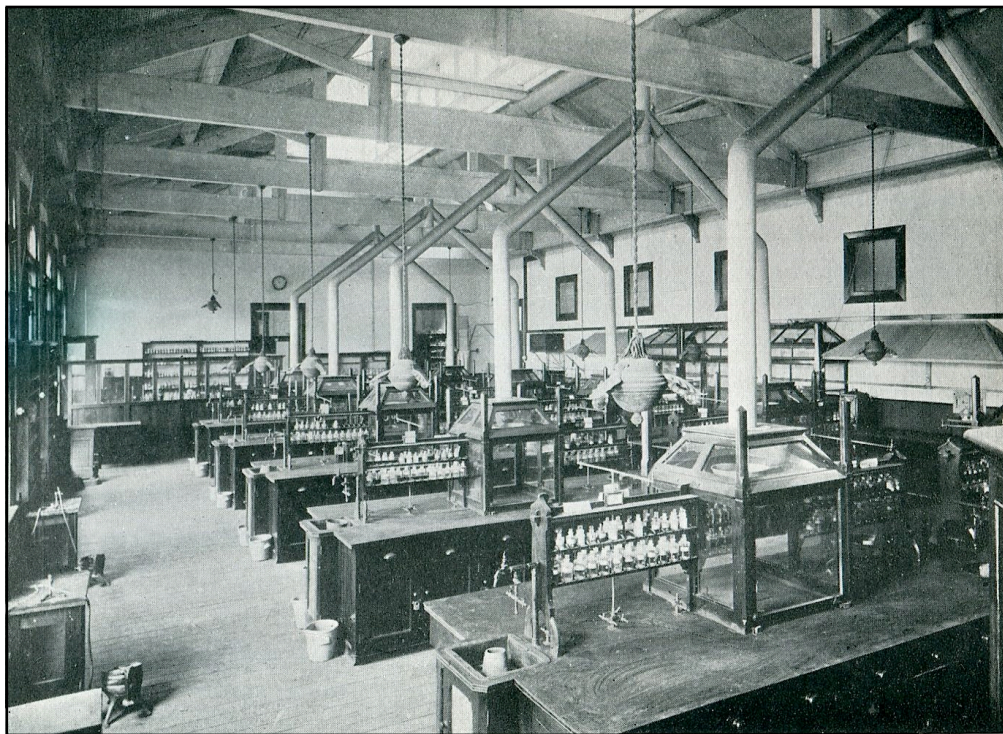


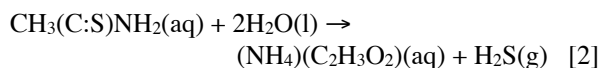
Figure 11. The laboratory for qualitative analysis at the University Sydney, circa 1916. Each hydrogen sulfide hood could accommodate four students, two on each side. Also note the shelves of glass-stoppered reagent bottles above each work station.

metric HCl-FeS generators, directly into the laboratory. At the University of Sydney, in Australia, the spigots for the $\text{H}_2\text{S}(\text{g})$ were located at the individual lab benches (figure 11) and were each surrounded by a small glass fume cupboard (42), whereas at the University of Wisconsin, in the United States, the gas spigots were located in special communal side hoods and had automatic shutoff valves to guard against careless students walking away after failing to turn off the $\text{H}_2\text{S}(\text{g})$ supply (43). At Sydney the central gasometer or generator was located outside under a lean-to, whereas at Wisconsin it was located in the basement. The author recalls historian Aaron Ihde telling him that this basement location led to the death of at least one janitor who was responsible for recharging the generator and who was found dead on the floor of the room after having been overwhelmed by the toxic gas.

A second approach to the hydrogen sulfide problem was to replace the gas with alternative and more easily manageable solid or liquid sources of sulfide ion, usually in the form of various organic thio compounds. The literature on this approach was summarized as early as 1909 in a small monograph published by Donath (44). The alternative sources discussed by him included ammonium thioacetate, ammonium dithiocarbonate, and ammonium dithiocarbamate, as

well as such inorganic sources as disodium thiosulfate and disodium sulfide. Also included in the monograph were various alternative qual schemes based on the use of these reagents.

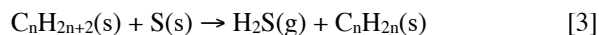
To the best of my knowledge, none of these alternatives were ever widely adopted in the teaching of qualitative analysis, and it was not until Barber and Grzeskowiak recommended the use of thioacetamide in 1949 that this approach finally had a significant impact (45). This compound is stable in water at room temperature but above 80°C rapidly undergoes hydrolysis to give hydrogen sulfide and ammonium acetate:



Thus it was an ideal choice for the *in situ* generation of small quantities of hydrogen sulfide like those required by the semi-micro schemes that were rapidly displacing the more traditional macro approach by the late 1940s and early 1950s. Though articles exploring yet other organic thio compounds continued to appear (46, 47), thioacetamide quickly became the reagent of choice and was soon the subject of articles in the educational literature recommending its use (48, 49). Only when its potential carcinogenic properties were revealed

in the 1980s was the initial enthusiasm moderated (50).

As early as 1938 yet a third method for generating small quantities of hydrogen sulfide was brought to the attention of chemical educators by Jackson and Suhrer (51). This was based on the dehydrogenation of long-chain hydrocarbon waxes upon heating them with elemental sulfur. Though the reaction is probably quite complex, the underlying idea can be summarized by means of the generalized equation:



and could be achieved by simply heating a mixture of paraffin, sulfur and an inert filler in a small test tube with an attached cork and delivery tube. Gas generation ceased when the heating was stopped and thus this arrangement could serve as a simple $\text{H}_2\text{S}(\text{g})$ generator for a course in semi-micro analysis. Indeed, as the above authors noted, by 1938 ready-made pellets of this mixture were commercially available under the trade name of "Aitch Tu Ess" and this is the method that the present author used when first learning qual in the early 1960s (52).

Yet a fourth and final approach to the hydrogen sulfide problem was to eliminate the use of the gas altogether. As early as 1869 Zettnow published a small laboratory manual in which both hydrogen sulfide and ammonium sulfide were replaced by such group reagents as sulfuric acid, zinc metal, barium carbonate, ammonium carbonate, and sodium phosphate (53), and in his 1909 monograph Donath described a similar sulfide-free scheme based on the use of hydrazine and hydroxylamine salts (44). Since World War I both the research literature (54-56) and the educational literature (57-61) have featured numerous hydrogen sulfide-free qual schemes, several of which have relied on simple organic reagents, such as ammonium benzoate (64) and phthalic acid (55), for group separations. Though several of these schemes were actually published as textbooks (62-64), they for the most part had no significant impact on the teaching of qual beyond the confines of the schools from whence they originated, thus illustrating once again the remarkable resiliency of the original sulfide-based qual scheme pioneered by Rose and Fresenius nearly 175 years ago.

Pedagogy

But far more important than issues of scale, advances in separation techniques, the introduction of tailored organic reagents, or the use or nonuse of hydrogen sulfide was the pedagogical issue of why qualitative analysis should be taught in an introductory chemistry course in the first place, and it was largely the failure

of chemistry teachers to reach a consensus on this issue that ultimately led to the subject's virtual demise.

This question was raised as early as 1928 by J. S. Guy in an article published in the recently founded *Journal of Chemical Education* (65). Guy felt that there were three possible reasons for teaching such a course:

1. To teach students the practical laboratory art of qualitative inorganic chemical analysis.
2. To serve as a training ground for the writing and balancing of chemical reactions.
3. To teach the basic principles of chemistry as exemplified in the laboratory by the aqueous solution chemistry of the common metals.

Though the first of these objectives was most certainly the one adopted by all 19th-century courses in qualitative analysis, Guy felt that it was no longer appropriate for a 20th-century introductory college chemistry course, though he grudgingly acknowledged that it might still have some value for mining and engineering schools.

Indeed, this motive for teaching qual was rejected in far more specific terms by Louis P. Hammett of Columbia University (figure 12) in his manual of qualitative analysis, published the next year. As stated in his preface (66):

This book is not an attempt to teach an immediately useful practical art. A properly conducted course in qualitative analysis does teach much valuable analytical chemistry, in the sense of general principles, typical methods, and some experience in technique. But this is not a practical art, and cannot be so as long as we must exclude elements as common as tungsten and vanadium lest the course become too time consuming.

In other words, the selection of metals covered in the standard qual course was both limited and artificial, and this failing alone made it of little use to the modern-day analytical chemist. Nor was it possible, Hammett went on to point out, to correct this defect by including more elements in the scheme as this rapidly made the course too lengthy and too complex for the average freshman. In fact, Noyes and Bray had published a complete qual scheme for all of the known metals two years prior to the appearance of Hammett's book and even a cursory glance at its more than 500 pages of detailed laboratory instructions and tables quickly confirms the truth of Hammett's observation (67).

The second objective listed by Guy probably strikes the modern teacher as eccentric, but it was a re-

flection, as he noted, of what often happened on quizzes and exams in a typical qual course and so became, in practice, the actual objective of the course even when not considered to be so in theory.

It was the third objective that Guy fully endorsed, arguing that the laboratory course should be coupled with lectures dealing with such topics as the theory of ionic dissociation, the laws of equilibrium and mass action, the colloidal behavior of precipitates etc. This was in fact the essence of Ostwald's famous 1894 monograph on the foundations of analytical chemistry (20), but by 1928 this classic was largely unknown to the newer generation of chemistry teachers. However, its lessons had already been taken to heart by several authors of qualitative analysis manuals, among whom Guy singled out for special mention the pioneering 1911 textbook by Julius Stieglitz of the University of Chicago, noted above (22).

An even better example of this approach, however, was Louis Hammett's 1929 manual, mentioned earlier, which bore the title *Solutions of Electrolytes with Particular Application to Qualitative Analysis*. The order in which the topics are listed in this title is of great significance since, as they suggest, Hammett viewed qualitative analysis as but one way of illustrating the more general topic of the physical and chemical behavior of aqueous solutions of electrolytes (66):

This book is based upon the belief that a course in qualitative analysis is an ideal method of presenting and of illustrating by copious examples the general principles relating to the behavior of solutions of electrolytes; and that this part of physical chemistry is an indispensable part of the preparation for advanced work in chemistry and for the study of medicine and engineering. It is an attempt to make the fullest use of qualitative analysis as a means of teaching chemistry.

It might be thought that the change in objectives advocated by Guy, Hammett and others finally resolved the pedagogical debate and that, with this turn of events, the standard course in qualitative analysis had successfully identified a new and worthwhile teaching objective that assured it a continuing place in the chemical curriculum. Yet this was not to be the case. A mere 25 years after the appearance of Hammett's book, we read the following comments by the British analytical chemist Cecil L. Wilson (68):

No teacher of inorganic qualitative analysis who has made any attempt to remain abreast of movements within the subject during the past few years can ignore the uncertainty that exists regarding its precise function in the training of chemists. The "solution" to the problem adopted by some teachers, particularly in the



Figure 12. Louis P. Hammett (1894-1987).

United States of America – to drop the teaching of qualitative analysis quietly out of the course – is no solution, but is rather an evasion of the issues involved.

Implicit in these comments is a reversion to the first of Guy's three objectives – namely that an introductory course in qualitative analysis should reflect current, rather than traditional and largely outdated practices, in analytical chemistry. A possible solution to this problem, in Wilson's opinion, was a complete revamping of the course based on an aggressive application of new specific organic reagents and drop analysis as outlined in the English translation of the book for which his comments served as a foreword – the 1954 volume, *Qualitative Inorganic Analysis: A New Physico-Chemical Approach*, by the French analytical chemist Gaston Charlot (68).

The Charlot book was ambitious to say the least and went far beyond the simple use of drop reactions as confirmatory tests that had been advocated in the earlier schemes of van Nieuwenburg and Davis (27, 28). Rather Charlot believed that he and his coworkers had identified a series of specific colorimetric tests, based on the use of new organic reagents, the use of masking agents, and the proper adjustment of pH and other reaction conditions, which allowed one to dispense with virtually all separations and to directly test an unknown for each cation individually (69). As for the book's "new physico-chemical approach" this appears to have consisted of the qualitative use of a series of either concentration-pH or E_h -pH plots to determine

optimal reaction conditions.

An objective look at the book quickly reveals that it lacks the organization and detailed laboratory directions required for an introductory course directed at freshmen and would in fact prove something of a challenge even for a first-year graduate student. More serious is the fact that, by dispensing with separations, it also eliminated one of the most important intellectual aspects of a traditional qual course – the logical application of a sequence of specific reactions to attain a predetermined goal. Rather surprisingly, none of the authors quoted above called attention to this aspect of a qual course, though it was the feature that the current author found most compelling when first learning about qualitative analysis back in the 1960s (52).

Teaching students to select and logically apply a sequence of organic type reactions to achieve the synthesis of a specific compound from a given set of starting materials is considered to be an important part of intellectual training in organic chemistry, yet precisely the same kind of training was implicit in the sequential application of standard ionic reactions to achieve the separation and identification of a given set of cations. Indeed, application of this training formed the culmination of many qual courses in the form of the so-called nine-bottle problem in which students were given a list of nine solutes and nine unlabeled solutions and asked to formulate a sequence of reactions using only the solutions in question that would allow them to deduce which solute was in which bottle (70, 71). In sharp contrast, Charlot's collection of specific cation tests leaves one with the impression that they are dealing with a collection of magic recipes. However convenient and efficient for the practicing analytical chemist, they seem devoid of any larger intellectual lesson for the introductory student.

Yet a second problem with spot tests that rely on a heavy use of specially designed organic reagents is that they subvert the use of the qual scheme to teach the descriptive and theoretical solution chemistry of simple inorganic compounds, such as chlorides, nitrates, oxides, hydroxides, carbonates, and sulfides, as well as simple coordination compounds. The manner in which the qual scheme could be used for this purpose was illustrated in great detail by A. F. Clifford's 1961 text, *Inorganic Chemistry of Qualitative Analysis*. In his preface to this 500-page textbook, Clifford outlined the assumptions of such an approach (72):

It has been long recognized by instructors of undergraduate chemistry that there is little need to teach qualitative analysis for its own sake. Actual analyses are very seldom carried out in this manner any longer. It is nevertheless true that the classical analytical

scheme is one of the best vehicles ever devised for teaching the systematics of inorganic chemistry. The purpose of this book, then, is not to teach methods of analysis, but rather to give as thorough a grounding as possible in the chemical relationships in the periodic table on which the classical analytical scheme is founded. This is done in terms of trends in solubility, trends in acidity and basicity, trends in oxidizing and reducing power, and the like. In order to accomplish this intelligibly, such topics as electronegativity, oxidation potentials, and the equilibrium principle are treated, the last extensively.

Clifford also went on to make the points outlined above concerning the pedagogical consequences of the overuse of organic reagents and spot tests (72):

The laboratory procedures have been selected for their pedagogical worth rather than for their analytical utility. For example, the detection of strontium is accomplished with a saturated calcium sulfate solution in order to demonstrate the trend of solubilities of the alkaline-earth sulfates, rather than, for example, by complexing calcium with triethanolamine which, from the analytical point of view, is more satisfactory but which teaches very little. For the same reason, the use of organic spot test reagents has been reduced to a minimum to emphasize inorganic reagents which perhaps are less satisfactory analytically but which nevertheless illustrate fundamental inorganic chemistry better.

Fade Out

Though 32 years after its publication, Laing would attempt to revive the descriptive inorganic approach to qual advocated by Clifford in his textbook (73), the timing of the original book's publication could not have been worse. The 1960s saw the beginnings of a major change in the nature of the introductory university chemistry course whereby it was transformed from a traditional course in descriptive inorganic chemistry into a baby physical chemistry course. The newer generation of freshman chemistry teachers was less and less interested in teaching the details of basic descriptive inorganic chemistry, let alone in illustrating it in detail in the laboratory. The qual course had traditionally consumed an entire semester of freshman laboratory. Now more and more schools either eliminated it altogether or truncated it to a single experiment in which either the analysis of the silver group or some version of the nine-bottle experiment was used as a "representative example."

The consequences of this change were brought home to the author in the early 1980s during his first

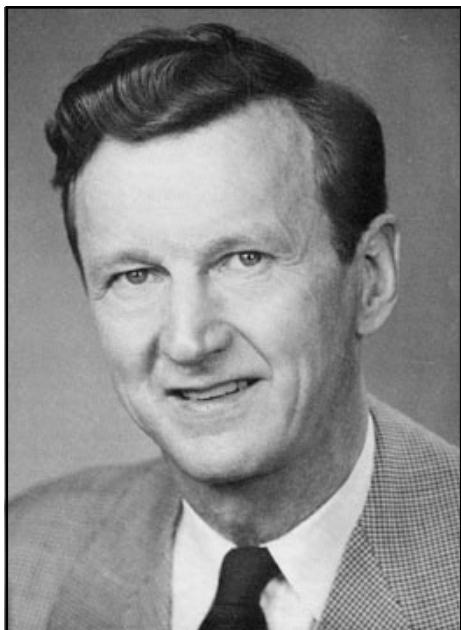


Figure 13. C. Harvey Sorum (1899-1986).

teaching job. I was lecturing on the origin of Werner's coordination theory to a senior class in inorganic chemistry and observed that the difference in the behavior of chloride ligands in the first versus the second coordination sphere of a metal complex was easily demonstrated using the standard chloride test. I had naively assumed that every chemistry student knew that the standard analytical test for the chloride ion was to precipitate it as silver chloride, but to my horror I found myself instead facing a roomful of blank stares. Something in the chemical universe had changed and that something was directly traceable to the disappearance of the standard qual course.

At present very few schools teach an entire semester of qualitative analysis and the plethora of qual manuals characteristic of the late 19th century and the first half of the 20th century is no more. One of the very few American qual manuals to survive this upheaval is the volume by C. Harvey Sorum of the University of Wisconsin (figure 13). This volume can be traced back to a macro qual manual first published by Louis Kahlenberg and J. H. Walton in 1911 (74). By 1922 at least four editions of this text had appeared and, starting in 1937, it was continued under the authorship of Walton and C. H. Sorum for at least another 12 years (75). Finally, in 1949, Sorum replaced it with a manual of semi-micro qualitative analysis which he saw through four editions before being joined by Joseph Lagowski of the University of Texas-Austin (figure 14) for the 5th edition in 1977 (76, 77). Lagowski, in turn, has seen the book through

three more editions, the last of which was published in 2005. Thus this book has a history spanning more than a century or almost as long as that of the classic text by Fresenius.

When interviewed in 2010, Lagowski touched on his reasons for continuing to teach qualitative inorganic analysis (78):

I know that qualitative analysis is not very popular with many teaching chemists today, but I like the subject because it allows students to learn about descriptive chemistry in an interesting way. That is, students can be trained to do simple manipulation techniques in the laboratory – measuring, mixing, observing, estimating – in the context of a simple unknown. For example, given access to the substances hydrochloric acid, aqueous solutions of sodium carbonate, silver nitrate, and sodium hydroxide, all in unmarked containers, place the appropriate correct labels on the containers. You may recognize this “qual problem” as a version of the 10 solution experiment.

In many ways these reasons are similar to those voiced by Louis Hammett more than 75 years earlier and which are as valid today as when they were first written (66):

The most valuable thing to be gained from a scientific education is the ability to find things out by experiment. Descriptive experiments whose results can be foretold by reference to the textbook are not good examples of scientific method, and it is precisely to the



Figure 14. Joseph J. Lagowski (1930-2014).

most intelligent students that they are most tiresome ... It is the great virtue of analytical chemistry as a teaching instrument that it sets problems which can only be answered by experimentation.

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