Analytical Chemistry in the United States, 1830-1850

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The period between 1830 and 1850 was a witness to a great advancement in the field of chemistry. During this period there occurred a profound change in the position of chemistry as an individual science. The greater part of the advancement was due to the European chemists, who were the leaders in the field at that time; however, the American chemists made their own definite contribution to this growth and development.

The advances were made equally in the theoretical and practical aspects of the science, as well as in the educational field. By necessity, analytical chemistry was a leader at this time. The chemist of the day was dealing with the unknown, and in order to establish anything he had to turn to the analytical approach. It is quite reasonable, therefore, that the analytical chemists should stand out as some of the important leaders.

The following discussion is an attempt to give recognition to a few of the outstanding analytical chemists of the period, and to compare their conditions and techniques to ours. Undoubtedly many men whose contributions are also noteworthy have been omitted from this short discussion. The men discussed are a few of those whose publications in the volumes of the *American Journal of Science* lend confirmation of their prominence. Some of the biographical material has appeared in the *Amercan Chemist.* **(1).**

The equipment with which these men labored leaves much to be desired when compared to that which is now available. Their lack of chemical glassware, burners, and other simple pieces of common laboratory equipment makes their circumstances seem primitive by comparison. They relied heavily upon blowpipe analysis and frequently considered a smell test as sufficient proof for positive qualitative detection. Counterpoised filter papers were combined for a filtration, and after the precipitate had been dried in the paper, the individual pieces were separated, one again serving as the counterpoise. Washing of a precipitate frequently required 12 hours and the drying of a precipitate on a sand bath was sometimes continued for days.

Many of their procedures are very similar to current ones. A double dehydration of silica with hydrochloric acid was common technique, as was the precipitation of calcium as the oxalate. The methods of precipitation of iron, aluminum, and magnesium were very similar to ours. This list could be extended to many other techniques common to both periods.

The activities of the analytical chemists fall into two distinct categories; general and special. These categories develop quite naturally from the fact that some men occupied themselves with complete analyses of samples, whereas others were interested mainly in some specific analysis or determination. Such a classification gives a nearly equal division of the work done.

The "general" classification embodies analyses of mineralogical, coal, meteoric, coral and agricultural samples. That such a large proportion of the activities of the time should be devoted to this type of work is quite understandable in the light of the fact that the expansion and exploration of the United States was still the major national endeavor. It seems logical that the analyses necessary to support the numerous geological surveys and investigations initiated during that period should be a very important contribution of chemistry to its environment.

One of the outstanding mineralogists of the day was Charles Upham Shepard whose "Treatise on Mineralogy" was a handbook for many years. Dr. Shepard, who was located at the Medical College of the State of South Carolina, contributed much to the analytical chemistry of the times with his numerous publications containing minerological analyses.

At the same time, Augustus A. Hayes had obtained a reputation as an outstanding analyst, and his works appear in collaboration with geologists and mineralogists who brought their samples to him for analysis.

Charles T. Jackson also contributed much to this literature. He contributed even more to analytical chemistry when he founded the first laboratory for instruction in analytical chemistry in Boston in 1838.

The list of men recording complete analyses would be long, and would include the following men and their interests: Walter Johnson, coal; Benjamin Silliman, Jr., coal and coral; John C. Norton, Lewis C. Beck, and Robert Peter, agricultural.

The classification of "special" work includes many interesting developments by American chemists. The interests of the group are widely varied, ranging from the use of special reagents to the refinements of analytical technique as it was known at the time. In many cases the developments were meant to be aids to the performance of complete analyses; which, whether published results appear or not, represented the major field of activity of the analytical chemist for reasons outlined above. In many cases we find men contributing to both categories.

Dr. Charles Jackson belongs to the latter group. In addition to the work already mentioned, he was interested in the detection of arsenic, particularly in connection with poisoning. In his discussion of the Marsh test, he mentions obtaining a sensitivity of one part per million, an exceptionally good test for that period. The detection of gold is also included in a list of his interests.

Dr. J. Lawrence Smith, whose current reputation is due to his method for the decomposition of silicates and subsequent determination of the alkalies, received his M.D. degree and became a leader in the field of chemistry during this twenty year period, although his above-mentioned work did not appear until somewhat later. Working in Charleston, South Carolina and abroad, his interests were many and varied. He early reported the use of potassium chromate as a reagent for barium in the presence of strontium. His investigation included a search for a reagent to selectively dissolve the precipitates, and as a result he obtained a confirmatory test for barium if the precipitate did not dissolve in acetic acid. This desire for a greater certainty in qualitative testing exemplifies one phase of the development of the scientific thinking of the period. He followed this type of work in showing the use of CaF_2 as a test for fluoride ion rather than the usual etching of glass. In the early forties Dr. Smith became interested in the action of neutral salts on each other. He investigated many examples and presented theories for their explanation.

Perhaps Dr. Smith's article most interesting to analytical chemists is his 1843 contribution concerning a new instrument for the analysis of carbonate-containing materials. In this he describes with accompanying drawings a vertical glass tube with a portion graduated from 0-100 from bottom to top. The lower end of the tube is drawn out into a tip. Entitling this tube a "calcarimeter", he proceeds to describe in minute detail the procedure one should follow in making an acid solution and standardizing it against a sample of a pure carbonate. This is followed by details for evaluating an alkaline solution against the standard acid, and the subsequent procedure for diluting each solution in order to give a concentration which will give a more convenient reading. The necessary steps for the determination of an unknown carbonate sample are then described. Again these are done in minute detail. He even describes another tube with only three calibrations which was used for adding the excess acid. The third calibration is designed for adding an additional portion of acid in case one goes past the litmus paper end point.

It is of interest that Dr. Smith controlled the flow by placing a cork containing a glass tube in the top of the buret and regulating the addition with his finger in the manner in which we now use a pipet. He also demonstrated his modern insight by his discussion of the fact that his procedure had the further advantage that it could be performed with good accuracy by untrained personnel. He even includes data obtained by persons who had no training and were told just which steps to follow.

This investigation did not show whether this is the first buret described in the literature, but it seems to be one of the first applications of our present day "back-titration". Dr. Smith was well versed in the chemical literature of the day. He served for some years as a foreign correspondent for the *American Journal of Science* while he was in Paris, and he did considerable abstracting of foreign articles for the same journal. It seems quite reasonable that a man who was a leader in his field and so well informed in his field would not have gone into such detail to describe the instrument, the preparation of the standard solutions, and the procedures involved if they were not new. His other articles do not follow such a pattern.

Many advances in classical analytical technique were due to the efforts of William B. and Robert E. Rogers. These two brothers came from a family in which the father and four sons were all active in the field of chemistry. The two mentioned made much more of a contribution to analytical chemistry than the others, however. Initial evidence of their interest in carbonates was shown in a paper dealing with an improved instrument for the determination of carbonate: a weighed system in which the flask, acid, and samples were weighed prior to mixing and after evolution of carbon dioxide. This article in 1844 was followed in the next two years by others which dealt with an application of the instrument to the study of the decomposition of minerals and rocks by carbon dioxide-containing waters and the absorption of carbon dioxide by solutions.

Their works are all characterized by an outstanding insight into the errors involved. They were meticulous in their dedication to detail. They pointed out to the leading German chemists that they were ignoring a serious error due to adsorbed water vapor in the system, and therefore used thorough drying trains in conjunction with their experiments. They considered the errors due to adsorption of gas by the corks and the fallacy of handling the apparatus with bare hands. They suggested that the work should be done at a constant temperature so that wiping of the apparatus was not required, since electrostatic charges were developed in so doing. These few examples only serve to represent the nature of their valuable contribution to chemical experimentation techniques, and to illustrate the advance in the thinking of the time. It was this line of thought which contributed greatly to the change of chemistry from a philosophy to a science.

.Professor W. W. Mathers at West Point contributed to the chemistry of the day with the determination of the ratio of the constituents in aluminum chloride and aluminum oxide. In the latter he pointed out to Berzelius that his values were incorrect and that his ratio was the inverse of the true one. He also presented a unique determination of silver in an ore following cupellation. He worked from a standard curve relating the size of the globule and the amount of silver.

Professor Robert Hare at the University of Pennsylvania was undoubtedly one of the most energetic thinkers of the period. The literature at that time is full of his letters to Berzelius, Faraday, and other leaders concerning points in their current theories or interpretations with which he could not agree. His development of new apparatus for the analysis of air and the purification of carbon monoxide carried him into the analytical field.

One could easily extend this reminiscing to volumes, but this consideration will terminate with having mentioned only a few of the better known men. Professor J. W. Bailey deserves mention for his insight into qualtitative analysis as early as 1837. The first few paragraphs in his communication deal with the way in which reagents function. He defined, but left unnamed, the functions "selective" and "specific". The addition of these terms would make his writing appropriate in any modern text. Dr. Lewis Feuchtwanger did some very early work on the reactions of arsenic; which, accompanied by a number of colored illustrations, stands out in the 1830 literature.

Having considered the men, their thinking and works, there remains one rumination which binds the whole together; education. Chemistry in 1830 was not an entity. It was not taught as an individual science. It is reasonable that in view of the prominence of analytical chemistry, the analytical chemist should have a great deal to do with the development of instruction of chemistry. Thus, Dr. Jackson's laboratory of instruction in Boston in 1837. Also Benjamin Silliman, Jr., a student of Jackson, and Joseph P. Norton founded in 1847 what became known as the Yale Analytical Laboratory. It is significant that although this laboratory was conducted in a Yale University building, the founders paid rent to the University for its use; and they furnished from their own private funds all expenses for equipment, supplies, and salaries connected with the operation of the laboratory.

That such conditions should have been a part of our educational history is unfortunate. However, the advances made by the analytical chemists of the period did much to hasten the acceptance of chemistry as a science which deserved recognition in our educational system. The following tribute to an analytical chemist has appeared in the literature (1): "The Massachusetts Institute of Technology owes the conception and successful inauguration among science teaching institutions of America almost solely to the personal efforts of Professor William B. Rogers".

In these many ways, analytical chemists and analytical chemistry, as yet unrecognized as such, contributed to the development and recognition of the science of chemistry between 1830 and 1850.

Literature Cited

1. SILLIMAN, BENJAMIN. 1874. American contributions to chemistry. American Chemist 5,70.