REVIEW.

SOME THOUGHTS ON THE PRESENT CONDITIONS OF ANALYTICAL CHEMISTRY.[1]

By W. F. Hillebrand.

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It is a natural and a justifiable belief that with the progress of time we learn to do better the things that a while since were new and strange—this both singly as individuals and collectively as nations. When the great advances our country has made in the domain of chemistry within the past twenty years are contrasted with the conditions obtaining before that time, particularly as regards facilities for acquiring a sound chemical education, it seems quite reasonable that we should feel that analytical chemistry has kept pace with the general advance, and that our chemists are now not only more numerous by far, but also, taking them collectively, more capable analysts than their predecessors. But it were unsafe to accept such a belief as fact without some stronger evidence in its support than the existence of a general law of progress.

It is difficult, if not impossible, to make comparisons that will admit of deciding favorably or adversely the point just raised. But happenings of the past two or three years have thrown a flood of light upon the present condition of analytical chemistry in some lines of technical work, and the illumination comes as a distinct shock to the recipient, who may justly ask: If the conditions are so in these branches, is there any reason to suppose them better in others?

When evidence is forced upon our attention, giving rise to doubt and uneasiness, it behooves us to examine the evidence with care and, if found convincing, especially if reinforced from varied sources, to face the problem boldly with a determination to ascertain the causes of failure and the proper remedies to be applied.

The evidence to which I have referred, it is needless to recapitulate at this time. Much of it has been presented in the reports of a committee of the New York Section of the Society of Chemical Industry bearing on the analysis of cements and copper slags. Additional testimony appears in the report, published in the Journal of our Society for December, 1904, of the Committee on Uniformity in Technical Analysis, of which I am chairman. Much might be added to that which has appeared in print. The volume of evidence is large and its character of such a kind as to force one to the unwilling belief that the frequent charges of bad work are fully substantiated. The

[1] Read at the Philadelphia Meeting of the American Chemical Society.

causes for this condition are, however, but imperfectly understood, and until ascertained the corrective treatment cannot be outlined with any degree of precision.

It is nothing new for chemists to differ in their analyses of the same material, and they will never cease to differ by reason of human fallibility and the limitations of all analytical methods without exception, but unless two chemists are able to assay or analyze the same sample with results acceptable as a basis for buying and selling, the analysts suffer in the estimation of those interested in the transaction. If similar want of accord is of frequent occurrence, the burden of blame may be shifted and the art of analysis, even the science of chemistry itself, fall into disrepute among the unthinking. In any case the matter is one of grave concern in many ways, and merits the serious consideration of chemists as a body.

Many causes for such inability to arrive at concordant results have been set forth and discussed often by others, both here and abroad, notably by Messrs. Dudley and Pease, and Baron Jüptner von Johnstorff, with special reference to the iron and steel industry. The unsatisfactory conditions in iron and steel laboratories were not new then, for those interested had long been confronted by the most annoying and disturbing lack of agreement in the returns by different chemists. The same was doubtless true in other lines of work, though, because of the lesser magnitude of the industries involved, the notoriousness was less. What efforts were made through an international committee to correct the state of affairs as regarded iron and steel chemistry is matter of history, and need not be here entered upon. Neither will the long and still continuing work of the agricultural and food chemists at home and abroad to better their own condition by a close comparative study of methods and the selection of standards be more than alluded to, nor is it my object, on the basis of their results, to advocate the adoption and general use in technical lines of standard or uniform methods of analysis. My main object is to force upon the attention of chemists the seriousness of the present situation, a situation which is little creditable to our profession.

We may analyze the causes for the variations shown in the analyses of the same, or supposedly the same, samples, and, neglecting the inevitable personal factor, find that in certain cases the sampling was incorrect, in others that the water was bad, the reagents faulty, their effect on the glassware used greater than had been suspected, or that of several methods for reaching the same end one or more are of doubtful value unless used with that knowledge which can only come of long practice, sharpened by discriminating judgment. But in the ultimate analysis these distinct causes nearly all lead back to one stem root—some defect in the early education of the chemist—for which the institutions that are yearly sending forth young chemists supposedly fitted to do good work in their chosen lines, are responsible.

It will, of course, be asked: In what respect have their instructors failed toward these young men? A definite and comprehensive answer to this demand it is out of my power to give. I am pretty fully convinced, however, that the teaching of incorrect methods is neither wholly nor in large part to blame. The faults, if faults there be, are rather those of omission than of commission. Let me suggest a few possibilities and leave each one concerned to be his own judge of their fitness. In so doing I disclaim all thought of reflecting upon any particular individuals or educational institutions. Some may be, and doubtless are, less at fault than others, and the results are perhaps in most cases not due to ignorance or indifference so much as to causes quite beyond their control. The condition is none the less existent and demands earnest attention. I speak, of course, not as an educator and, therefore, not as one qualified to dictate in the matter of ways and means. But, I repeat, a certain condition confronts us, and this condition needs a remedy. Where there is a determined will backed by a united sentiment, most obstacles can be overcome with time. It is this determined will and sentiment that I would help to arouse to action, not only among those of you who are teachers, but among all others as well, for the former will be strengthened in their efforts, if they have behind them the good will of the great body of chemists.

In what I shall say I may seem to take issue in one or two matters with the views recently expressed by a distinguished foreign teacher and investigator, but the difference, I surmise, is more on the surface than fundamental.

Many inquiries addressed to the participants in one series of analyses elicited the information that few knew anything definite about the quality of the water they were using, though examination showed it to be bad in a few instances and on the border line in others. Still less was known as to the quality of the reagents, except that they came from reputable firms. One admitted that a flaky sediment showed in his ammonia bottle, but he used only the clear liquid above. If the sediment represented silica from the bottle, as may well have been, what had become of the other constituents of the attacked glass unless they were in solution?

Now why were these things possible unless because it had never been sufficiently impressed upon them in their student days that without proper tools to work with, among which water and reagents are first to be considered, good work is impossible? You doubtless do not fail rightly to tell them that absolute accuracy is unattainable in analysis, but do you make it plain that approximation is possible and that it will be the closer the greater the care bestowed upon the tools and at every step of the analysis itself?

Is a student ever required to find out by actual test how good his water is and both the kind and amount of its contamination, if such there be? Is it customary to instruct him in the testing of his reagents and as to the character of the contaminations to be looked for in all of the more important ones, or is he allowed to go forth with the impression that the label C. P., while not a flawless title, is a sufficient guarantee for all the demands of technical analysis? Is he, in fact, ever cautioned to find out, by actual test, the errors with which his work may be affected, due to imperfections in his tools of the kind just mentioned? And that without such knowledge and the ability to make correction for the defects, or the courage to fight for better materials with which to do, he will occupy a false position with respect to himself, his employers and the community at large?

My experience of the past few years has convinced me that in these respects, at least, much is neglected that should not be neglected in the curricula of our colleges. It seems to me that if instruction in such fundamental essentials is not thoroughly drilled into the budding chemist, so that it becomes for him as much a matter of course afterwards to look to the quality of his tools as it is to weigh out his sample before analyzing it, he has received a scant equivalent for his years of study, and that he has good grounds of complaint against his alma mater if he comes to grief by reason of her neglect.

Is the student's work ever checked against material of which the exact composition is known? I do not refer here to such things as simple salts, but to more complex bodies like limestone, cement, zinc ore or slag, in which many separations have to be made and all constituents should be determined. Is the student in such analyses religiously required to test the purity of his precipitates and the completeness of his precipitations by a careful examination of the filtrates? And is he taught that a satisfactory summation does not imply correct separations? Or that closely agreeing duplicates are not proof of good work?

Only by such exercises can the young worker gain any knowledge as to his own power to do good work, and acquire that proper confidence in himself which is so essential.

Just here the committee which I represent may be, perhaps, of some assistance in preparing for distribution, either through its own agency or that of the Bureau of Standards when that institution shall be in position to lend permanent aid, large samples of various materials of which the exact composition will be ascertained. These will then be supplied on demand to all who may wish to check their own, or their students' or employes' work. It is the earnest hope of the committee that the invitation which it contemplates issuing to collegiate instructors will be met in a cordially receptive spirit, namely, to analyze or cause to be analyzed, by their most advanced students, a limestone of known composition which the committee will undertake to distribute. In this way can be acquired in a short time valuable information as to their own abilities or the skill of the young men they are sending into the chemical arena. Incidentally, the merits of the methods they teach will be tested.

Another point brought out by the recent series of zinc-ore analyses is the failure of many to exercise discrimination in the choice of methods for different classes of ore, they being seemingly ignorant of the fact that a method of solution employed in one case may be ineffective in another, or that the presence of so-called interfering elements may forbid the use of a method otherwise unobjectionable. Some seem to have made no effort to ascertain if such interfering elements were present. The committee on zinc-ore analysis, whose report is in small part published in this Journal, **26**, 1648, voices ideas similar to the above in the following words: "Instead of teaching analytical chemistry most of the schools teach what one instructor has well called 'cook-book methods,' that is, schemes of analysis which give the student no ideas of the principles of analytical methods, but make him think that the analysis of one kind of ore is something essentially different from the analysis of any other. One-fifth of all the analysts represented show the effects of this kind of teaching and either use methods which contain no means of separating manganese and copper on ores that contain large amounts of these interfering elements or use methods that will not decompose the ores at the start."

From what I am told regarding the ratio of instructors to laboratory students, there is in many of our institutions woful lack of supervision of the work of each individual student. I have little patience with the principle which in effect puts a book on analysis before a beginner and tells him to find his own way through the various analyses, with such help as he may get from his fellows and an occasional hasty call from an assistant. Circumstances, no doubt, often compel the following of this plan, but its adoption is, to my mind, little less than a crime against the learner. I believe it is held by some that the really good student will come successfully through this mill and the others fall by the way, but how much better off the good student would be, for more attention at critical periods seems to be left out of consideration. Facts seem to speak against the success of this theory. There are hundreds of little tricks of manipulation which the student cannot learn for himself and which he should be taught by a conscientious assistant, having little to do but devote his whole time to a limited number of workers. This brings me to the remark that no laboratory instructor should be required or allowed to do outside work, either for his superiors or himself, so as to encroach in any way upon the time that should be given to those under his supervision. This would necessitate a very decided increase in the corps of instructors, so as not to deprive them of opportunity for research work. Once the fundamentals have been mastered, the worker, correctly started, may well be left more to his own resources, but even then he should receive frequent visits for the purpose of guarding against relapse from right ways, for giving needed additional information, and answering the proper queries that are pretty sure to occur to a good student. It is far better that the student should learn to do comparatively few things thoroughly, mastering the whys and wherefores of every step, than a great many superficially and without acquisition of the underlying principles. It is only the one thus thoroughly grounded who is in a position to use or devise short cuts without great danger.

Doubtless many works chemists are compelled to labor under conditions which preclude the highest class of work. Dust envelops them and makes cleanliness impossible and a high grade of water and reagents useless, or such is the haste called for in order that the results shall be of use to regulate the daily running of the furnace or mill, that the highest or even a high standard is unattainable. Let it be admitted that even these crude results suffice to regulate and control the smelter charges, or the cement mixture and its finished product, yet no chemist who has to work under such disadvantages should permit himself to enter into analytical competition with those better situated in these respects without stating plainly the disadvantages to which he is subjected. Especially should he never undertake commercial analyses for pay, with which goes the implied understanding that the purchaser is to receive full value for his money. Moreover, even he who is so unfortunate as to be handicapped in the ways mentioned will be able to do better work than otherwise, if the foundations of his knowledge have been solidly laid.

Often, no doubt, the ignorance or indifference of the owner of the works is responsible for the distressful conditions under which the chemist labors. The young chemist is naturally disinclined to risk his place by a too determined opposition to existing conditions or by insistent demands for their betterment. The situation is unfortunate, and it is difficult to see how it is to be remedied except by the gradual growth of appreciation among employers that chemistry is a handmaiden worthy of far better treatment than she now receives, that she needs careful housing and feeding in order that she may give good work at all times. Possibly employers may, to some extent, be aided in reaching this enlightened state by the refusal of professors of chemistry to recommend students to accept positions where the conditions are known to be needlessly incompatible with satisfactory work.

Another condition in which I hope to live to see the beginning of a radical change, is that of the quality of reagents accepted and used unhesitatingly for most kinds of work, not merely technical in character. How often have I heard it said: Oh! this is good enough for technical work! Possibly it is for one kind, but it is sure not to be for some other. This necessitates either a multiplicity of grades of certain reagents or the need for special purification by the chemist, or, a commonly accepted alternative, incorrect results.

Let me emphasize this point by an illustration. The solubility of gold in nitrous acid has long been a disputed matter, yet an important one in assaying. Not long since a chemist sought to settle the question, and prepared nitrous acid from potassium nitrate. With this he effected solution of from 1 per cent. up to nearly 50 per cent. of the gold acted on, according to the temperature employed. No one seems ever before to have observed any such marked effect, and the experiments were repeated by Dr. E. T. Allen in the laboratory of the Geological Survey, care being taken to prepare the nitrous acid from a nitrate free from chloride. The result was that, despite the utmost care, no positive solvent effect on gold could be observed. The inference is that the nitrate employed by the author of the original statement contained chloride, which was almost certainly the case, if it was not an article of unusually high grade, such as is not likely to be found in an assay laboratory. To what extent, if at all, the author's instructors may be indirectly responsible for the harm that has been done by the dissemination of such erroneous information, it is, of course, impossible to tell. The harm has been done, however, and undoubtedly by reason of the employment of a low-grade reagent where one of exceptional quality was demanded. Unfortunately, the refutation which will shortly appear cannot entirely undo the mischief already spread.

Why cannot instructors come to a clear understanding that good work requires good tools and that this is quite as true in the rush of a works laboratory, unless conditions utterly debar cleanliness, as it is anywhere else? Why should they, unintentionally of course, lower in the minds of their young men the dignity of the work these latter have set out to do? Why not from now on, one and all, resolve to pursue a different course? By so doing you will render comparatively easy the task of the Committee on Purity of Reagents. Even as it is, one firm of chemical manufacturers in this country has announced to me its entire readiness to do its best to furnish reagents of the quality the committee may eventually decide to call for, and, unofficially, I have been told that a large importing firm will provide the reagents when the committee's specifications are known. It only needs concerted and persistent refusal on the part of the heads of educational laboratories to accept any but really good reagents to bring about before long a most radical change in the present situation regarding these most important tools of the chemist.

It is doubtless a fact that the ever-widening field of chemical application and the overwhelming multiplication of analytical methods make it more and more difficult to cover the whole field in any but a superficial manner in the time which it seems possible to give to chemical study, and hence render extremely obscure the solution by our chemical educators of the problems presented for their consideration. The difficulty is enhanced by the following condition: Chemists in charge of large industrial laboratories sometimes prefer young men not too well informed as to a variety of methods, but would have them come unfettered by preconceived notions and so ready to adopt, without objection, the methods in vogue in the particular laboratory. While a knowledge of many methods may be rather deprecated by their chiefs, a thorough grounding in general chemistry and the theory of analysis is, however, greatly desired by them in their young assistants.

On the other hand, the young man who is suddenly called upon to fill the sole chemical position in a mill or smelter, and upon whose work the successful running of the establishment may depend, would be sadly, if not hopelessly, handicapped were he equipped only on the theoretical side of his profession. How to avoid both horns of the dilemma and yet graduate our young chemists properly equipped and unimpaired in efficiency for their life tasks is a problem that is taxing and will long tax to the utmost the best efforts of our foremost chemical educators.

While I have thus endeavored to point out wherein our colleges may be more or less remiss, it is not for a moment to be asserted that they are altogether responsible for the present situation. There are other factors concerned, and among them is uncertainty as to the value or adaptability of many methods. Herein, the National Bureau of Standards, if its effective coöperation can be secured by a moderate grant from Congress, may become of great value in the testing and comparison of methods by men of experience, who are not so pressed for time as to be unable to check their results in manifold ways. The work of advanced students in the comparative investigation of methods is often excellent, though sometimes of more value as training to the student himself than to the public at large, but the average value of work of this kind must be enhanced by having it done by men of ripe experience, whose whole time can be devoted to it.

Let us then, for one thing, continue and extend the work begun over a decade since by the iron and steel chemists and now carried out by those engaged in the agricultural industries and in the examination of food products. It has been shown that the shoe pinches not only one or two toes, but several, and the remedy must be sought for and applied speedily before the injury becomes too great or incurable. We must not flinch at the prospect before us, but take up the task with stout hearts and a determination to get at the roots of the trouble that afflicts us, for there is more than one root, as I have already intimated, and then to apply the appropriate remedies.

It is most important that the educators of future generations of chemists ponder these matters and endeavor to devise ways for improvement, if not by concerted action, then by the efforts of single colleges.

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METHODS FOR THE COMPLETE ANALYSIS OF REFINED COPPER.

BY GEORGE L. HEATH.

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In 1894 Dr. H. F. Kellar[1] presented a paper on the analysis of copper as practised by him at that time, and similar condensed accounts on Montana methods appeared from the pen of Titus Ulke,[2] in 1899. In response to invitation, the writer will present the principal methods now employed in large technical laboratories, giving preference to those which are personally believed to be most delicate and accurate, condensing the account by references wherever possible.

Great accuracy, both in sampling and in chemical manipulation, is especially necessary in the case of copper on account of the precious metals it frequently contains, and on account of the marked effect which traces, even, of some impurities, have on its physical properties, and because of the liability of those impurities to segregation on cooling from a fluid to a solid state.

No technical chemist would now go through the tedious extraction of vast quantities of sulphide of copper as originally proposed by Fresenius. The present tendency is to take separate samples for the estimation of each group of foreign elements by some special method of isolation. Analytical results are usually carried out to 0.0001 per cent.

SAMPLING.

When copper is to be assayed for gold and silver, the material should be sampled direct from the molten furnace charges after thoroughly mixing and agitating the bath by the refining process.

A thin square plate, $6 \times 6 \times \frac{1}{2}$ inches, to represent the lot, is carefully poured from a full ladle. The size might be increased to $9 \times 9 \times \frac{3}{4}$ inches for very rich material. A set of five ($^5/_{16}$ inch) holes, drilled through the half-inch plate, will furnish an assay-ton (29 grams) sample for assay for silver and gold. The drillings from one hole of $\frac{1}{4}$ inch diameter will give one sample for electrolytic copper assay. Duplicates are generally taken.

[1] *J. Frank. Inst.*, July, 1894; this Journal, **16**, 784 (1894).

[2] *Eng. Min. J.*, **68**, 727 (1899); "Mineral Industry," 1901, pp, 223 *et seq.*