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Notices of papers and communications for the meetings to be made to Edward George Ballard, Queen's Park, St. Helens.

UNIVERSITY COLLEGE, ASHTON STREET, LIVERPOOL.

Wednesday, April 2nd, 1884.

PROFESSOR J. CAMPBELL BROWN IN THE CHAIR.

ON METHODS OF SAMPLING.

BY A. NORMAN TATE, F.I.C.

I was unable to attend the meeting of this section held last November, when a discussion took place on "International methods of sampling and testing Commercial products"; but in a letter addressed to the Chairman, with reference to the circular of Dr. Lunge, I ventured to express the opinion that an International agreement as to the modes of sampling and testing might be arrived at.

In discussing this question, I consider that we should first, fully and fairly inquire into all the several principles involved in sampling operations; for certainly in the operation of assessing the value of Commercial products, sampling is most important, for if the sample does not truly represent the bulk all further work is valueless. I believe that when all details of the characters of the substances to be sampled, nature of packages, changes which the substance may undergo after packing, and the conditions under which sampling may take place, are properly considered, satisfactory methods of sampling can be defined.

Dr. Hurter remarked, when discussing the subject at the meeting referred to, "Sampling will probably have to be left to the intelligence of the sampler. Samples have to be drawn under so many difficult circumstances as to localities, accessibility, and packages, that a rigid rule could not be drawn up, which can be enforced at all times, and under all conditions." No person conversant with sampling would expect this, but it may reasonably be hoped that certain general rules, based upon the character of the substance sampled, and the conditions surrounding it under different circumstances, may be drawn up and acted on by persons specially trained as samplers. The difficulty now, so far as I see, lies in the fact that samples are drawn too often by persons without any knowledge or appreciation of the characters of the substances to be dealt with.

It may be well to mention some few well-known substances, and the conditions surrounding their sampling, so as to point out some leading principles which, in my opinion, should be attended to. When such substances are sampled, there are certain items leading to discrepancies which are of the same general character, as for example the presence of moisture, the proportion of which is too frequently overlooked. Other items have special reference to special substances. One preliminary that has to be considered is the time and place of sampling, so that if a special strength or quality is to be delivered, the place of delivery and mode of sampling there, shall be clearly

understood. As a matter of practical detail, this is not always to be accomplished, and oftentimes it happens that what might have been quite up to strength or guaranteed quality at point of delivery, may fall short at some later date.

With reference to the statement that samples should always be drawn by persons acquainted with the properties of the substances sampled there comes the question "Who is best qualified to draw samples?" I was surprised to find this question included in a discussion marked out a year or two ago for the members of the Institute of Chemistry, viz.:—"Should chemists sample?" As my answer to such an inquiry I would say that if a chemist desires his work to be really useful, he should take every possible precaution to ensure that the sample he tests represents what it is supposed to represent, and consequently should make himself thoroughly familiar with every minute detail that has to be considered before the sample can be properly drawn. At the meeting of the Institute of Chemistry, at which this subject was discussed, I was astonished to find some analysts propound the view that the chemist has simply to analyse the sample given him, and need take no note of the circumstances of its sampling. To such a view I strongly dissent, and would say, that it is essential that the chemist who makes the test should not only be able to analyse and devise methods of correct sampling, but if necessary be able to sample himself. This matter of preliminary sampling goes beyond the actual sampling from packages, having reference to the treatment samples may undergo before and after they reach the laboratory, until they are actually dealt with by the analyst. I fear that many well drawn samples are much altered in character in consequence of faulty treatment either in manner of mixing, averaging, or general treatment before the analytical process is commenced.

Referring to details that affect samples generally, I would mention as an example moisture. The fact that the amount of moisture existing at the time of sampling and at the time when the sample is presented for analysis may vary, is too frequently overlooked. Moist samples are not unfrequently presented to the analyst in paper parcels, or under other conditions which certainly must give rise to changes in the percentage of moisture. Amongst such samples are sugars, with the exception of beet-root, the samples of which are usually placed in well-sealed bottles. Samples of other sugars come to me in paper parcels with no protection against loss of moisture; so also sulphate of ammonia, nitrates of potash and soda, manures, many minerals, solid oils and fats, and in all these the proportion of moisture is an item of commercial account. I might add to this list considerably, but these substances will serve to show to practical men the fault I wish to point out.

Now as to the remedy. It would be no great difficulty, for any Committee, or other appointed body, to define that substances containing moisture should be so sampled that the amount they contain at time of sampling, may be correctly determined in course of analysis. Rules dealing with moisture should refer to sampling in wet weather, transit of samples uncovered or left in a damp atmosphere, and the placing in bottles or other vessels that can be securely fastened and made waterproof, and other items will suggest themselves to every practical man.

Again, whilst the substances which I have just alluded to lose, others may gain moisture, as for example, caustic soda, and caustic soda ash. These also should have their peculiarities carefully noted, and be dealt with accordingly. I would allude here to other changes that may take place owing to the hygroscopic properties of some substances. Much alteration may

occur in the outer layer of the sample as compared with the bulk, as for instance with caustic soda ash, and bleaching powder, whilst other substances which are not hygroscopic, may in wet weather become damp at points close to sides of package. In such cases the sampler should so sample that the sample is drawn from the entire bulk and not simply from the outer layer. One statement of a blunder made by a chemist who was called upon to sample, well serves to show what I mean. It had been arranged that a parcel of soda-ash should be sampled and examined by him. He proceeded to the works, and had the heads of two or three casks taken out; scraped off some of the immediately underlying ash, placed it in a bottle, took it away with him, and sent in his report. I need scarcely say that the parties to the dispute did not settle the matter on the basis of his report when the circumstances were made known to them.

Changes in transit owing to absorption of moisture from the atmosphere and other changes, cannot be eliminated from any discussion on proper sampling.

Again the physical condition of the sample must be noted. Are all the particles of the same size? If not, how far is it possible by proper riddling and weighing to note the relative proportions of lumps and smalls? In the case of many minerals, unless this is attended to, no proper average of the bulk can be reached. The same holds good with small lumps or coarse powder, and fine powder. I have in my hand a sample, contained, as you will see, in a small homœopathic tube, which was sent me by a chemist, who professes to examine commercial samples. This represents some 50 casks of caustic soda ash of rough character, with many large and small lumps and much fine powder. This so-called sample is not even powdered, with the object of getting something like an average, and if it had been most likely it would not have represented the bulk, and to bring such a sample before anyone as the representative sample of 50 casks of soda ash is an instance of either ignorance or gross neglect of circumstances pertaining to proper sampling. An amusing instance of what I consider must have been faulty sampling, took place in the well known Birkenhead coffee-chicory case, when several members of the Town Council met together and weighed out and mixed quantities of chicory and coffee, and after mixing in their way, sent samples to different analysts, and chuckled over the reports received as showing how widely analysts differ. It is a matter exceedingly difficult, unless special precautions are taken, to ensure a thorough average mixture of ground coffee and chicory. And although it may have given these inexperienced Birkenhead town councillors some pleasure in chuckling over the results, the reason of the differences would be clearly enough apparent to those thoroughly experienced in the sampling and mixing of such substances.

There are other points connected with sampling based upon the mode of division. For example, it is not unfrequently the case that one or two pieces of barks selected at random are handed in as samples of many packages to be tested for quinine or other alkaloids. Such a mode of sampling is grossly faulty. Seeds will often afford better opportunity for taking samples from different parts of bulk so as to get a fair average, but owing to different sizes of seeds, and many other characteristics, really good samples are rarely obtained unless special precautions are observed. A case was before me not long since, when many particles of sand, gravel, and dirt of various kinds, were mixed with bones (the bones of course being the valuable substance), but not the slightest care was traceable in the selection of the sample, for after it had been drawn from bulk and divided into separate parcels, one parcel contained

bones fairly free from gravel, sand, etc., and another containing almost the whole of such matters that had been drawn from the packages. The chemist's aid was invoked to determine the amount of siliceous matter in the different samples, and any person conversant with the details of such examination will readily see how widely the results must have differed.

I might add many other examples of faulty sampling as conducted by commercial brokers and merchants; in fact the process of sampling as conducted usually in mercantile offices requires very careful investigation and revision.

There is another cause of error in sampling, and that is the tendency of the bulk to separate into layers, when solid matters in suspension in liquids subside, and are not fully mixed up before a sample is taken from bulk. No doubt many examples of such kind will suggest themselves to practical men. I have found this often in the case of liquid extracts used for tanning purposes. These without experience might be supposed to be of the same character throughout the contents of a cask, without any tendency to separate into layers, but, oftentimes there is a thick dense layer at the lower part of the cask, and a more fluid layer at the top. This has, I know, given rise to many discrepancies in the tests reported, respecting the so-called *same samples* by different chemists. These same extracts, if carefully watched during different methods of sampling, will afford good examples of changes in percentage of the more valuable constituent. Another example of layers is shown with palm oil. When packed in Africa it is sufficiently liquid to allow of solid impurities and water settling out before the oil becomes quite solid. It therefore follows that every special precaution should be taken to note under what circumstances, and in what parts of the cask dirt and water may be found, as it is usual, and of course desirable, for a deduction from the total weight of the contents of the cask to be made, so that only oil is charged for.

Certain circumstances connected with a process of manufacture may often lead to strange results in sampling, and frequently through carelessness. For instance in refining oil, the oil may be placed in the tank, from which it is packed, before the liquid or chemical with which it has been washed or treated has subsided. In such cases, whilst the greater number of the casks packed may contain a thoroughly good merchantable product, one or two casks may have a large admixture of water and other impurities.

Such facts as these, and others met with by practical samplers, suggest the question, "From how many packages should a sample be drawn?" That is, from the whole number, or if not, from what proportion of the whole number. In many cases it is desirable that the contents of every single package should be alike, in other cases this is almost impracticable, and is not absolutely essential, provided the variation is not great. On this point much may be said, and all interested in correct sampling will do well to give the matter most careful consideration. Circumstances surrounding the sampling of commercial products often prevent the sample from being drawn from the whole of the packages, and, therefore, unless there is great uniformity in the strength and character of the contents of each, a really good average is not attainable. At the same time it may be fairly said, that no one package of any particular lot of goods, should vary widely from others. Persons accustomed to sampling on board ships, on flats, in railway trucks, in warehouses, and other places, will, I think, fully appreciate the difficulties I have just alluded to.

There are many other points I might mention with examples, concerning the sampling of very many other raw materials and manufactured products that I have

for sampling in all trades. A twenty-five years' experience of sampling a substance in which accuracy of sampling was of the very first importance convinced him that there were three requisites for the sampler—integrity, experience, and brains. Whatever class of goods had to be sampled, men of integrity must be had in the first instance. Much mischief was caused in times past through roguery in sampling, and therefore an honest, upright man was the first essential. The next requisite was experience. To send a young chemist without experience of the particular article was a mistake. A man with practical experience was to be preferred to one with scientific training without the experience. Then, finally, they must have men with right-down common sense. Given these requisites of integrity, experience, and brains they could take samples.

Mr. H. TATE, jun., said it might be interesting to know that in the beetroot sugar trade they always sold on analysis. An association had been formed and a public sampler was appointed in London, in Liverpool, and in Greenock, by whom three samples of each lot of beetroot sugar were taken. One went to the sugar refiner, the other to the analytical chemist appointed by the association, and the third for reference. Thus all the samples passed through one man's hands, and he had a staff of samplers upon whom he could depend. Low sugars were not supposed to be sold by analysis. The association had only been formed two or three years, and it was found to work well. The samples they now got could be depended upon.

The CHAIRMAN said that where in the opinion of the analyst the sample was not a proper one, he ought to let that fact appear on the face of the certificate in some form or other. It would be easy to say that he had received such and such a sample, and that in his opinion it was not a good sample, or not in proper condition. For instance, if an article likely to give off moisture was delivered to him in brown paper instead of in a bottle, that fact ought to be stated, and its probable effect on the sample. He thought Mr. Allen had scarcely followed the argument as to written instructions. It was true that no written instructions could supply integrity, nor yet brains, but they would be useful, he thought, in imparting to others the experience of those who had gone before. He thought Mr. Carey had suggested the proper course to pursue—that was for a few skilled persons in the leading branches of manufacture to meet and draw up what they considered to be proper instructions both for sampling and testing, and submit those instructions to a central committee composed of one or other or all the three societies which had been named. He was sure they were all obliged and indebted to Mr. Tate for his paper.

REPLY.

Mr. TATE: As to the number of casks or parcels to be sampled in a cargo, cases had occurred to him where he had been able to draw samples from every single cask; and then there had been no disputes, the results of independent analyses being practically the same, and experience indicated pretty clearly that that was the best course of procedure. He saw no reason why the number of casks sampled should not be stated on the certificate, and he thought that if done, it would lead to some alteration in the mode in which parcels were sampled. He did not intend to suggest that the committee he had spoken of should lay down rules for guidance in every special case, but that such a committee should watch and press on improvements pertaining to sampling, and should have the power to nominate persons specially acquainted with certain trades and articles, to deal with any difficulties arising

in connection therewith, and draw up a set of rules for discussion and approval by the more general committee having charge of the whole question. Mr. Allen, he thought, had rather misunderstood him as to the employment of chemists as samplers. He agreed that it would be very wrong indeed to send a young chemist, an apprentice, perhaps, to sample a substance which he had never seen. Nothing could have been further from his mind; but chemists competent to analyse an article ought to be able to indicate how the samples should be drawn, and if necessary be able to draw them themselves. He was glad to hear what Mr. Henry Tate had said about the sampling of beet sugar; for that was the sort of thing he had had in his own mind. Here one trade dealing in one special substance had taken action to avoid disputes as to sampling; and by a very simple process appeared to have succeeded. The same or a similar system was what they wanted applying to a much greater extent. It was a practice which he almost invariably adopted himself, in analysing low sugars, to report the condition in which the samples reached him, and the probable loss of moisture, etc.; and that was what he thought analysts ought to do not only with sugar but with other substances.

DISCUSSION ON DR. HAMBURGER'S PAPER

May 7th, 1884.

MR. E. K. MUSEPRATT IN THE CHAIR.

Mr. J. FENWICK ALLEN: Dr. Hamburger deserves our thanks for his interesting and valuable paper. The subject he has introduced continues to be one of practical importance to the manufacturer, and is one on which we fear there is still a widespread ignorance and prejudice. Damage to vegetation is often attributed to chemical vapours, which is solely done by natural causes. Since our last meeting, a gentleman has been writing to the *Manchester Guardian* complaining that Dunham Park is being destroyed by the chemical fumes from Widnes and Runcorn. It seemed to me so extraordinary that noxious gases should prove so destructive at a distance of 15 miles, that I went over to investigate the matter, and I found no proof whatever of the least damage being done by the chemical fumes from the Widnes district. Many trees are dying, but from manifest natural causes, the most dominant of which are:—

1. Poor, shallow, sandy soil.
2. Drainage.
3. Bleak aspect.
4. Exposure by removal of sheltering trees.
5. Hard winters.
6. Age, natural decay.

Some years ago a farmer complained of his hedges being severely injured by the smoke from St. Helens. There had been a storm from the west, and the hedges on the side exposed to the wind were quite brown; but it happened that there were four hayricks standing at several yards interval from each other. Portions of the hedge opposite these ricks were screened by them from the west wind, but were not screened from St. Helens, which lay considerably more to the north of west. Wherever the hedge was screened it was green, whilst the portions opposite the gaps between the ricks were brown, just as was the remainder of the exposed portion of the hedge. During the last few days I have collected these specimens (specimens exhibited) of blighted thorns and injured rose trees. Looking at the trees I should have said they had been injured by chemical vapours,