

## NOTE ON THE ESTIMATION OF ALDEHYDES AND KETONES IN ESSENTIAL OILS AND ALLIED SUBSTANCES.

By HERBERT E. BURGESS.

*(Read at the Meeting, December 2, 1903.)*

THE importance for the analyst to be able to determine with a certain degree of accuracy any one, or preferably the chief, odour-bearing constituent of essential oils is so well recognised by those whose work principally lies in this direction that apologies are hardly necessary for bringing the present communication before the Society. The estimation of aldehydes and ketones in essential oils has always been attended with considerable difficulty, owing to many of the aldehydes themselves not being stable with the reagent used, and breaking down into various complex bodies which are themselves soluble in the reagent; and in some cases the other constituents of an oil are soluble to a considerable extent in the reagent used, thus making the percentage too high. In other cases, moreover, there is formed with the reagent a solid compound which obscures the meniscus to such an extent as to make the reading unreliable. The above remarks apply only to methods of direct absorption—*i.e.*, to the methods generally employed.

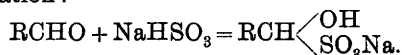
The various methods which have been suggested and adopted are as follows :

## ABSORPTION PROCESSES.

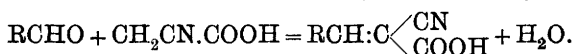
1. By treatment of the substance with a strong solution of bisulphite of soda or potash.

The directions for carrying out this process as prescribed in the various textbooks are as diverse as they are numerous, but the general consensus of opinion seems to indicate a strongly acid solution, and in some cases the presence of acetic acid; others, however, advise the use of alkalies, such as sodium carbonate. In considering these methods, it must, of course, be borne in mind that some are well suited to the preparation of the aldehydes or ketones in a state of purity, whilst others are better adapted for their estimation. The latter is the question which the present communication more particularly deals with.

The change which takes place with bisulphite of soda or potash is indicated by the following general equation :



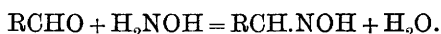
2. By a condensation product formed with cyanacetic acid in the presence of potassium hydroxide. The reaction that takes place for aldehydes is as follows :



3. By shaking the oil with a saturated solution of sodium salicylate. There seems to be evidence of the formation of a weak molecular compound, and with cinnamic aldehyde well-defined crystals have been obtained which give on analysis :

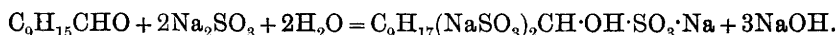
No.			Found.		Theoretical.
7.	Sodium	...	7.3	...	7.9
11.	Sodium salicylate	...	53.5	...	54.8

4. *Titration Method*.—By treating aldehydes or ketones with an alcoholic solution of hydroxylamine-hydrochloride, when oximes are formed, advantage being taken of the fact that the unused hydroxylamine may be easily titrated back. The reaction is shown in the following equation :



5. *Another Method, recently suggested by Hanus for Cinnamic Aldehyde*.—By treatment with an aqueous solution of semioxamazide, when a crystalline semioxamazone is formed, which is filtered off, dried, and weighed.

6. The method to which particular attention is now directed, and which gives accurate results with nearly all aldehydes and ketones generally met with, is carried out by heating the oil containing aldehydes or ketones with a neutral saturated solution of sodium sulphite, a soluble sulphonate being formed. In the case of citral the following reaction takes place :



Advantage is taken of the fact that an alkali is quantitatively liberated, and may, by adding an indicator such as phenolphthalein, be used to determine the end of the reaction.

The details for using the first three methods can be found in various memoirs, and a description of the same as particularly applied to the estimation of citral is given in the *Journal of S. C. I.*, December, 1901. Since that date the sulphite method has been further investigated, and found to apply equally well to most of the essential oils containing either aldehydes or ketones.

The objections to the use of methods Nos. 1, 2, 3, 4, and 5, are :

1. The very long time required for shaking ; the difficulty of determining when all the aldehydes are combined ; the impossibility of reading the meniscus with accuracy, owing to the insoluble crystalline mass, often accompanied with resinous bodies, floating at the division of the liquids.

Dr. Berté states that by using the potassium salt he gets good results with citral in lemon oil, and can obtain 7 to 7.5 per cent.

2. This method invariably gives too high results, especially with oils containing high percentages ; no clear meniscus is formed.

3. Oils containing different percentages of aldehydes and ketones require different treatment with regard to the quantity of hydroxylamine and bicarbonate

of soda required, and no definite instructions for the use of the process can be prescribed which will apply to all oils.

Substance.	Weight Taken.	Bicar-bonate Soda.	Mol. Bicar-bonate.	Hydrox-ylamine Taken = c.c. $\frac{E}{10}$ NaOH.	Hydrox-ylamine Used.	Time of Heating (Minutes).	Per-centage.
Benzaldehyde ...	1.034	0.4	0.5	124	91	30	93.3
„ ...	1.039	0.8	1.0	124	94	30	95.9
„ ...	1.037	0.8	1.0	378	85	60	86.9
„ ...	0.935	1.1	1.5	378	79	30	89.6
„ ...	0.900	1.0	1.5	150	75	60	88.3
Carvone ...	1.411	0.8	1.0	378	90	30	95.7
„ ...	1.410	0.8	1.0	378	83	60	88.9
„ ...	1.408	1.1	1.3	378	89	30	94.8
„ ...	1.346	1.0	1.3	150	80	60	89.2
Caraway oil ...	2.135	1.0	—	150	78	60	54.8
Citronellal ...	1.276	0.35	0.5	124	40	30	48.3
„ ...	1.308	0.7	1.0	124	61	30	71.8
„ ...	1.320	1.1	1.5	378	50	30	58.3
Cuminic aldehyde	1.442	0.4	0.5	124	91	30	93.4
„	1.459	0.8	1.0	124	93	30	94.3

4. The objection to this method lies in the fact that not only aldehydes, but nearly all oxygenated constituents, are absorbed by this reagent; but it will give, under definite conditions, figures of considerable value in essential oils containing mixtures of alcohol, esters, and aldehydes with terpenes, which will apply to all cases.

*Estimation in Essential Oils by the Sulphite Method.*—With regard to the determination of aldehydes and ketones, essential oils may be conveniently divided into two classes—those in which the estimation is made directly on the oil, and those in which the amount is too small to allow of direct estimation, but where preliminary concentration is necessary, such as citron, lime, lemon, and orange oils. In cases in which direct estimation on the oil is possible, the procedure is as follows: Five c.c. of the oil are introduced into a 200-c.c. flask, having a neck graduated to 5 c.c. in  $\frac{1}{10}$ ths of a c.c., with a side tubulus reaching to the bottom of the flask for introducing the oil, reagents, and water. To the measured oil is added a saturated solution of neutral sulphite of soda and 2 drops of ordinary phenolphthalein solution; it is then placed in a water-bath and thoroughly shaken, when a red colour is quickly produced. It is carefully neutralized with 1 to 10 solution of acetic acid until, after the addition of a few drops of acid, no further colour is produced. The oil is then run up into the graduated neck, and when cold carefully read. The difference between 5 c.c. and the reading will give the amount absorbed, and this multiplied by 20 the percentage.

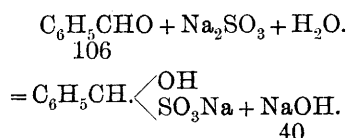
The following are results obtained by this process; in each case the substance has been further carefully examined, both chemically and physically, and in all cases represents a pure or commercially pure article:

ALDEHYDES, KETONES, AND OILS ON WHICH A DIRECT DETERMINATION CAN BE MADE.

*Oil of Almonds (Bitter).*—The method answers well in the case of this oil.

*Benzaldehyde.*—The chief constituent of oil of almonds is completely absorbed, even in the cold, giving a clear solution. Experiments made on a mixture of pure benzaldehyde and limonene which had been carefully redistilled over sodium several times gave theoretical results.

Reaction seems to take place according to the following equation :



The following data are confirmatory :

Took 5·3 grammes benzaldehyde and 12·6 grammes of crystallized sodium sulphite (theoretical amount) and titrated with N acid. Required :

Exp.			NaOH.		Calc.
1	...	44·2 c.c.	= 1·8 grammes	...	2·0
2	...	45·6 „	= 1·82 „	...	2·0

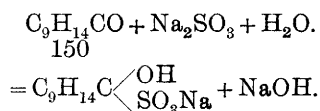
Well-defined crystals are formed in the neutralized solution on standing. On examination they proved to be identical with the ordinary bisulphite addition product, as the aldehyde is again liberated by the addition of acids or alkalies.

*Anisal.*—Gives theoretical results and a clear solution. Mixtures of pure aldehyde and limonene gave theoretical results.

*Caraway Oil.*—The method will be found very useful for this oil, the only convenient test for the valuation of the oil up to the present being its specific gravity, from which is calculated the percentage of carvone present, on the assumption that the oil only consists of limonene and carvone. But this is not sufficient to detect adulteration.

Some recent oils gave by the method 55 and 57 per cent.

*Carvone*, as may be inferred from the above, is readily absorbed by this reagent, giving theoretical results. A similar reaction to that which occurs in the case of benzaldehyde probably takes place with this ketone :

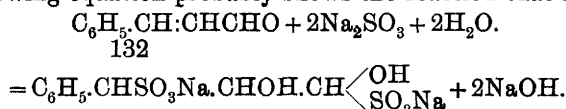


Took 7·5 grammes carvone and titrated with N acid. Required : 49·4 c.c. = 1·98. Calculated 2·0 grammes NaOH.

*Cassia and cinnamon oils* both give good results. Large amount of phenolphthalein required.

For *cassia oil* some figures recently obtained are 80 and 85 per cent. ; and for *cinnamon oil* (genuine), 68, 74, and 72 per cent.

*Cinnamic aldehyde*, the chief constituent of the above oils, also gives theoretical results. The following equation probably shows the reaction that here takes place :



Took 3·3 grammes of aldehyde. Required 46·5 c.c. N acid = 1·86 NaOH. Calculated 2·0 grammes. The same reaction probably applies in the case of citral and citronellal and all olefinic aldehydes.

*Citral*.—As has been shown elsewhere, the method answers well, giving theoretical results.

*Citronellal* forms a milky solution, and at first is very frothy. Consequently, care must be taken that none is lost through this cause. The reaction takes a considerable time and heating to complete the reaction, but gives good results.

*Oil of Cumin*.—Litmus solution will be found a better indicator for this oil. A genuine oil gave 24 per cent. cumic aldehyde.

*Cumic aldehyde* at first forms a solid compound, but on heating with the addition of acetic acid goes into a clear solution. Litmus should be used.

*Oil of Dill*.—In the case of this oil the method will be found extremely useful, as the carvone may be estimated with accuracy. A recent distillation gave 50 per cent.

*Oil of Lemongrass*.—The method with this oil works remarkably well, giving a sharply-defined meniscus. It has been shown by Parry that acetone is sometimes added to make the oil pass the solubility test. This would also show as aldehyde by the absorption method. Shaking the oil with water, or determination of its refractive index, will, however, at once indicate oils thus sophisticated.

*Oil of Pennyroyal*.—With this oil phenolphthalein does not act well as an indicator. Litmus is better. A recent oil gave 16 per cent. pulegone.

*Pulegone*.—

*Oil of Spearmint*.—The method is valuable in the case of these oils and works well, giving a clear solution. Genuine oils give about 62 per cent. carvone.

*Oils of Tansy, Thuja, and Wormwood*.—The method is useless for these oils, for the reason that thujone, the active constituent of these oils, does not form a compound with the reagent.

*Nonyl and Decyl Aldehydes*.—Considerable time and heating are required to complete the reaction with these substances, but good results may be obtained.

*Oils in which a Direct Estimation of Aldehydes and Ketones cannot be made*.—In this class there are only four of importance—viz., citron or cedrat, lemon, hand-pressed lime, and orange oils—and it will be convenient to consider the estimation of citral in lemon oil first, as the same method and remarks will apply in many respects to the other three oils.

*Lemon Oil*.—As this oil contains only a small percentage of total aldehydes, and consists chiefly of the inodorous hydrocarbon limonene, it is necessary to carefully fractionate out the hydrocarbons, and, while doing this, the analyst may come to a more definite knowledge of the genuineness of the oil if the following procedure be adopted.

The method, as particularly applied to lemon oil, was first suggested in a paper read before the Society of Chemical Industry in December, 1901, and since that time has been further investigated as a general method for other oils of a similar type, and for convenience is again described.

Having first determined the specific gravity at 15° C., the rotation in a 100-millimetre tube by sodium light, and the refractive index at 20° C., the oil is next distilled, and this, if carried out carefully, will show any adulteration. One hundred c.c. of the oil to be examined are put into a distilling-flask having three bulbs blown in the neck, and fitted with cork and thermometer. This is connected to a condenser with a suitable receiver, having two vessels graduated at 10 c.c. and 80 c.c. respectively. A Brühl's apparatus answers the purpose very well. The whole is exhausted, and a pressure of not more than 15 m.m. should be obtained. The flask is now gently heated by means of an oil-bath, and 10 c.c. distilled into the first tube. The next vessel is then put into position and the distillation continued until 80 c.c. have distilled over. The pressure is now relieved, and the residual oil in the flask distilled over with steam. The quantity so obtained should be carefully noted. Then the differences in rotation and refractive index of fraction 1 and those of the original oil will indicate added turpentine; fraction 2, lemon terpenes; fraction 3, the total amount of oxygenated constituents—*i.e.*, terpeneless oil and the amount of aldehydes.

The aldehyde should be estimated on this fraction after the above two constants have been taken in exactly the same manner as previously described. For example, supposing 7 c.c. of oil were obtained for the third fraction, and that, of the 5 c.c., 2.1 c.c. were absorbed in the aldehyde determination, the percentage of citral in the original oil would be  $\frac{2.1 \times 20 \times 7}{100} = 2.9$  per cent. A few remarks here as to the percentage of citral contained in lemon oil may not be out of place, especially as the subject is one that has recently been the cause of dispute among several essential-oil analysts.

The percentage given by this method is somewhere about 3 per cent. for genuine oils, whereas, up to some four years ago, 7 to 7.5 per cent. was the only figure that could be recognised as compatible with a genuine oil.

This higher percentage is still maintained by some analysts, both English and Italian, although there is no known method that will give directly or indirectly a figure anywhere approaching this percentage. The facts admitted on all sides are:

1. That a genuine oil does not yield more than from 5 to 6 per cent. of concentrated, *i.e.*, terpeneless, oil.
2. The oxygenated constituents in the 90 per cent. or so of terpenes distilled are less than 1 per cent.
3. A concentrated oil never contains more than 50 per cent. of aldehydes, the average being 46 per cent.

On the face of these facts, admitted by all experts, it seems inconceivable that any analyst should maintain a 7 per cent. standard, as, taking an oil yielding at the highest 6 per cent. of concentrated oil, only half or 3 per cent. of this would be of an aldehydic nature.

Such guaranteed 7 per cent. oils must, of necessity, be very misleading to con-

sumers and manufacturers, and tend to place the analysts in a very false position, as on such certificate a manufacturer of concentrated oils would expect a yield of 12 per cent. at least of terpeneless oil; but, as above mentioned, this is not the case.

*Hand-pressed Lime Oil.*—The method as above described for lemon oils is equally useful for the determination of citral in this oil, which should contain about 8 per cent. of this constituent.

This distillation method would at once show the addition of lemon or orange oil.

*Citron or Cedrat Oil.*—Consists chiefly of citral and limonene (*vide* ANALYST, October, 1901). The same method of distillation may be used. A genuine oil should contain about 4 per cent.

*Oil of Orange.*—This oil consists chiefly of limonene and a small quantity of decylic aldehyde. The distillation method is useful in detecting adulteration with cheaper oils of the citrus series.

The rotation of the first 10 c.c. should always be higher than that of the original oil, and the aldehydes may be determined on the third fraction. A typical sweet orange oil gives about 0.75 to 1 per cent.

In conclusion, I wish to express my thanks to the proprietors of the London Essence Co., in whose laboratories this work has been carried out, for time and material placed at my disposal, and for valuable analytical work and suggestions by Mr. T. H. Page, B.Sc.

#### DISCUSSION.

The PRESIDENT (Mr. Fairley) having invited discussion,

MR. ERNEST J. PARRY said that, of the questions dealt with in this paper, probably the most important was that of the percentage of citral in lemon oil. The lemon-oil industry was one involving very large commercial interests. Many tons of lemon oil which was guaranteed by certain analysts in Messina and in London to contain 7 per cent. of citral were annually imported into this country, but it had never been found possible—although many representations had been made—to obtain an official statement of the methods of analysis yielding the results upon which such guarantees were based. He desired to draw special attention to this, since in his own experience—and, he believed, in that of other analysts also—trouble repeatedly arose in regard to samples of lemon oil, because, although 7 or  $7\frac{1}{2}$  per cent. of citral was guaranteed, it was found impossible to return more than from 3 to  $3\frac{1}{2}$  per cent. When Mr. Burgess and Mr. Child some two years previously communicated to the Society of Chemical Industry their paper on the subject, he had been inclined somewhat strongly to oppose their views as regards the percentage of citral in lemon oil, and had considered the true percentage to be much higher than they believed it to be. At that time he was using a process involving distillation of the oil under reduced pressure and determination of the citral in the last 10 or 12 per cent. by absorption with cyanacetic acid. Mr. Burgess had hinted that the results yielded by the cyanacetic acid method were too high, but Professor Tiemann, Messrs. Schimmel, and he (Mr. Parry) himself had found that the process gave very accurate results under certain conditions. He found, however, that unless the cyanacetic acid used was absolutely fresh very erroneous results might be obtained, owing, probably, to the



cyanacetic acid undergoing some molecular change on keeping; and to that cause he attributed the fact that the results he had then obtained—namely, from 5 to 6 per cent.—were too high. A large amount of published work had shown 7 per cent. to be an impossible figure. Mr. Burgess had examined probably some thousands of samples, and he (Mr. Parry) had examined a very large number in absolutely identical apparatus with that now described, and he could confirm Mr. Burgess's results in every respect. Turning to other matters referred to in the paper, he had found that, in the estimation of cinnamic aldehyde in cassia oil by the bisulphite process, reading was always rendered difficult by the collection of resinous matters in a layer beneath the meniscus. This was not of much importance in practice, seeing that the amount absorbed was at least 70 or 75 per cent., but he would like to hear whether by the use of the monosulphite the presence of the resinous layer would be done away with. He understood that this would be the case. Absorption processes generally, from a theoretical point of view, were incorrect, for, apart from the actual chemical reaction, it was necessary to take into account the equilibrium of the solvents. For instance, the same sample of clove oil would yield different results with different strengths of caustic potash, and in no case would there be an absolute absorption of the eugenol with the whole of the caryophyllene left floating at the top, for it was always possible to extract with ether from the soap solution a further quantity of the hydrocarbon which had dissolved in it. Errors from such causes as this were most accentuated in processes like that of Berté, in which the terpenes were not first eliminated by distillation, but if the terpenes could be eliminated free from citral the errors due to secondary causes were so slight as to be of little importance. He agreed with Mr. Burgess that the maximum amount of citral lost in the terpenes was 0.2 per cent., and an allowance for a loss of that amount was always made in his own analyses. It was, moreover, an established fact that no ordinary lemon oil could be made to yield more than about 5 per cent. of terpeneless oil, and not much more than half of this was citral; so that, for there to be 7 per cent. of citral in the original oil, at least 4 per cent. must be lost in the terpenes—which had never yet been shown to be the case. If such a loss really did occur, there would be no difficulty at all in detecting it, for in the case of orange oil, although the amount of citral present was very small indeed, he had been able, after concentration, to separate well-defined crystals of citryl- $\beta$ -naphthocinchonic acid having a sharp melting-point. Consequently it would be quite possible to detect the presence in the terpenes of well under 1 per cent. of citral. He had rarely met with any pure lemon oil that conformed to the British Pharmacopœia requirement that the rotation of the first 10 per cent. distilled should not differ by more than 2° from the rotation of the original oil, and, in his opinion, any sample fulfilling that condition must usually be heavily adulterated.

Mr. J. F. CHILD said that, when this distillation method of the estimation of citral in lemon oil had been originally brought before the Society of Chemical Industry by Mr. Burgess and himself, the figures given for the citral content of the third fraction were worked back to give the percentage of citral in the oil itself, but it was not suggested that this was absolutely correct, but only an indication of the probable amount. From lemongrass oil practically the whole of the citral could be fractionated, but in



the case of lemon oil this was not possible; in fact, it was impossible to obtain a fraction containing more than 78 per cent., for some decomposition always occurred. So in the present case also there must be some small loss due to decomposition—not much, perhaps, but certainly more than Mr. Parry or Mr. Burgess had allowed for. He thought it amounted probably to about  $\frac{1}{2}$  per cent.

Mr. T. H. PAGE said that one of the most satisfactory results they had obtained with this process had been the fractionation of a large quantity of terpeneless lemon oil and the determination of the percentage of citral by the sulphite process in each of the fractions. The fractions were small, so that the citral content, except in the first and last few, was nearly the same. In practically all cases consistent results were obtained. In a few cases there were discrepancies of 1 or 2 per cent., but this could only be expected with an absorption process; but this was certainly better than with any other he had used. Moreover, in the case of mixtures containing known quantities of citral, the results obtained completely bore out the calculated proportions.

Mr. CHAPMAN said that the new and really important matter brought forward in this paper was the application of the sulphite method, which had been described some time ago by Mr. Burgess in reference to the estimation of citral in lemon oil, to a large number of other essential oils containing aldehydes and ketones. The process certainly marked a very great improvement on the older bisulphite extraction method, as the reaction appeared to be fairly quantitative, and to be capable of measurement by the formation of alkali, which marked the completion. In the acid sulphite process, in which one simply shook a measured volume of the oil with a saturated solution of sodium bisulphite, it was necessary to experiment with known mixtures, and to assume that after a certain number of shakings and after heating to a certain temperature the extraction was complete. There was one point which Mr. Burgess had not alluded to—namely, the chief reason given by Dr. Berté for the substitution of the potassium for the sodium salt, which he (Mr. Chapman) believed to be that a clear solution of all the aldehyde compounds was obtained, and consequently there was no troubled meniscus, but quite a sharp line of demarcation between the two liquids in the measuring tube. He had not himself, however, been able to test this point, and therefore did not know whether the claim was a correct one. The situation at present existing with regard to the determination of citral in lemon oil was certainly one which he thought was almost unparalleled in the history of analytical chemistry. A number of chemists who were interested in the analysis of essential oils had made very careful examinations of lemon oil and of solutions of citral in redistilled hydrocarbons by several methods, and the results for genuine oil of lemon had invariably fallen very far short of 7 per cent. of citral; while, as Mr. Burgess had mentioned, manufacturers working on a large scale had found themselves unable to obtain anything like 7 per cent. of citral from the oil. Nevertheless, as Mr. Parry had remarked, it was agreed that the hydrocarbons obtained were practically free from citral. Where, then, did the remainder of the citral go to? He certainly thought that those chemists who maintained that 7 per cent. was a correct proportion ought to state in detail the processes by which they arrived at their results. No such statement, however, had hitherto been made, with the single exception of a brief note

recently published by MM. Berté and Soldaini. Very large commercial interests were involved, and those chemists who were unable to obtain such high results as 7 per cent. were placed in a somewhat unpleasant position. He must say that he could not see that the particular apparatus now shown possessed any advantage over the one which had been previously described before the Society by himself and Mr. Burgess. Among the advantages which he thought that apparatus possessed over Dr. Berté's was the small tube at the bottom, which enabled fresh liquid to be run in and the exhausted liquid to be run off, the whole contents of the flask being thus maintained under far more complete control than was possible in a long tubulated flask. Then, again, 25 c.c. was for obvious reasons a far better quantity to work on than the 5 c.c. used by Dr. Berté. In connection with the valuable distillation process for which Mr. Burgess and Mr. Child were responsible, he had carried out side by side duplicate experiments on the same oil, as far as possible at the same rate of distillation, and yet had met with pretty wide differences in the optical properties of the corresponding fractions. Possibly Mr. Burgess, with his greater experience, might be able to get more definite results, but his own experience had been that it was unwise to draw too definite conclusions from the figures obtained for the separate fractions.

Mr. ALLEN said that it used to be considered that aldehydes formed with bisulphites definite substances which were constant in character. These bodies, however, were now known to be sometimes very complex, two or even three different compounds being capable of being produced from the same aldehyde, according to the sulphite used, and apparently according to the strength of the sulphite solution. All these were circumstances which tended to shake one's faith in absorption-processes as ordinarily carried out. He was glad to think that Mr. Burgess had been able to ascertain the composition of the products formed from the amount of alkali set free in the reaction. Personally, he had a very limited confidence in the composition of commercial sulphites, for so-called sulphites of the alkali-metals were sometimes largely sulphates, and contained very variable amounts of actual sulphite. Perhaps bisulphites were better. The potassium metabisulphite was probably the most constant product. He would, however, like to have Mr. Burgess's assurance that he knew the exact composition of the sulphite used, because such knowledge would add very much to the ease with which other chemists could repeat his experiments. The whole subject of essential oils was one of great interest, and when experts differed to such an extent as was sometimes the case it was quite time that the reasons for such differences were fully known. He had no sympathy with chemists who were not prepared to explain their processes to others, and who preferred, although they maintained the accuracy of their results, to keep their processes secret.

Mr. BURGESS, in reply, said that the cyanacetic acid process was a somewhat complicated one, and he was glad to know that Mr. Parry had succeeded in obtaining good results with it. He (Mr. Burgess) thought that the reason for the production of a clear meniscus in cassia oil when sulphite was used was simply the fact that the resinous bodies were then contained in the unabsorbed portion of the oil, whereas when bisulphite was used they formed a sort of emulsion with the crystals of the

double compound which always remain undissolved. It was quite true, as Mr. Child had said, that there might be a loss of citral during fractionation, but even if it were as much as  $\frac{1}{2}$  per cent., that would not bring the results materially closer to the  $7\frac{1}{2}$  per cent. which was maintained to be present. There could be no doubt that some loss did occur in that way, although the point had never been brought forward until Mr. Child had mentioned it on this occasion. Although this discussion had rather turned upon the question of citral in lemon oil, the object of the present paper was, as Mr. Chapman had said, really to show that the method was applicable to many other substances. With regard to the apparatus, it had been stated by Dr. Berté and by others that, if the particular apparatus in question were used with potassium bisulphite,  $7\frac{1}{2}$  per cent. of citral could be obtained. He (Mr. Burgess), however, and others also, had not been able to obtain higher results than  $4\frac{1}{2}$  or 5 per cent., and it must be borne in mind that even here there was a considerable amount of solubility of the terpenes in the reagent used. The apparatus devised by Mr. Chapman and himself was certainly for many reasons preferable. In the first place, the multiplication error was reduced to one-fifth of that in Dr. Berte's process, and it was much easier to get the temperature the same each time—an important point, since these determinations were all made by volume. The small apparatus he had himself devised was merely a modification of the Hirschsohn flask, with a tubulure reaching to the bottom, so that there was no chance of the oil coming up, and water could be let in very gently to raise the meniscus. He had found no difficulty in obtaining good crystals of sodium sulphite of composition represented by the formula  $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$ . The metabisulphite could always be obtained of pretty constant composition.

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