Contents.

THE EXTRACTION OF CAFFEINE.

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I. SOURCES OF CAFFEINE.

The chief raw materials used in the manufacture of caffeine are tea damaged in transit and ' tea waste ' which consists of tea fluff, the hairs of the leaf bud of the tea plant, mixed with small quantities of coarse leaf and foreign matter from the floors and walls of the tea factories, which are swept down at intervals. About six million pounds of the latter material are exported from India annually, mainly to the United States, and, as the bulk of this appears to be used for making caffeine, the production from this source alone must amount to some 120,000 lbs.

Other raw materials which have been suggested as possible commercial sources of caffeine are tea bush prunings and the juice which is obtained when rolling or pressing very moist leaf,[1] but as these materials are not suitable for export, and the question of the manufacture of caffeine in India has only recently been considered, no attempts have yet been made to use them on a commercial scale.

Numerous analyses of tea are on record, but the literature contains practically no references to tea waste, or, as we prefer to call it, tea fluff. Table I gives the results of caffeine determinations in a few samples of fluff from different parts of India. The analyses were made on the undried samples, which contained in most cases 10 to 11 per cent. of water, for, although tea fluff is ' fired ' in the process of manufacture, it readily absorbs moisture.

TABLE I.

Caffeine Content of Samples of Tea Fluff.

Name of Estate	Locality	Elevation in feet	Average annual rainfall in inches	Caffeine per cent
Dejoo	Assam	200	145	3·06
Kaniamallai	Travancore	5,000	150	2·93
Attareekhat	Darrang	850	83	2·85
	Calcutta market	...	...	2·58
Ruttonpore	Cachar	60	110	2·41
Bonami	Travancore	4,000	...	2·40
Madupatty	Do.	5,500	80	*a*2·23 *b*2·24
Arcadia	Dehra Dun	1,800	75	2·19
Chittavurrai	Travancore	6,500	60	1·86

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[1] *G. N. Barooah, Ind. Pat.* 4619 1919.

There appears to be no relation between the caffeine content and the locality or elevation at which the tea is grown, but it would seem from the few examples given that a high rainfall tends to increase the quantity of caffeine.

The caffeine content of tea varies from 1·5 to 4·0 per cent. and very occasionally exceeds these limits, but average teas contain from 2·5 to 3·5 per cent. of caffeine.

Very few figures are available as to the quantity of caffeine present in parts of the tea bush other than the leaf, but an interesting collection of results has been made by P. A. du Pasquier.[1] As the original papers from which these were taken are in most cases not readily available, some of the figures, which appear to represent the most probable values, are reproduced in Table II.

TABLE II.

Caffeine Content of Various Parts of the Tea Plant. (Du Pasquier)

PART OF PLANT	PER CENT. OF CAFFEINE
Wood of root	0·0
Bark of root	0·15
Wood of stem	0·06
Bark of stem	0·08
Branches	0·0
Stem between fifth and sixth leaves	0·5
First leaf or bud	4·92
Second leaf	3·27
Third leaf	2·64
Fourth leaf	2·47
Fifth leaf, old and fallen	0·91
Hairs of young leaves	2·2
Corolla	0·8
Calix	2·4
Pollen	0·4
Manufactured flower tea	1·2
Tea seed shells	0·06
Cotyledons	0·10

The above values represent isolated determinations, and must therefore be regarded only as a rough indication of the quantity of caffeine present. In several cases higher values have been given, and one author in particular states that he has found 0·7 per cent of caffeine in the small branches, 0·2 per cent. in the roots and 2·0 per cent. in fresh seeds, but it is doubtful if these figures can be regarded as reliable. The majority of the results shown in the table including those

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[1] *Inaugural Dissertation Eidgenossischen Polytechnikums.* Zurich, 1908.

for the various leaves, were obtained by the author of the paper. The actual estimations were very carefully made, but the tea plants examined were grown on the Borromean Islands in Lake Maggiore, and it is doubtful if similar figures would be obtained from tea grown in the tropics.

We have examined two samples of prunings from 'Assam' and 'China' tea plants grown on Glenmorgan Estate, Nilgiris, at an elevation of 6,500 feet with an average annual rainfall of 50 inches. The leaves were stripped from the stems and the caffeine in them estimated separately after drying. In the case of the 'Assam' plant the stems were separated into 'thick' (4 to 10 mm. diameter) and 'thin' below this size. The caffeine was extracted by means of boiling water and prolonged extraction was found necessary.

The following results were obtained :—

'Assam' plant.	Leaves	1·09 per cent.
	Thin stems	0·40 ,,
	Thick stems	0·13 ,,
'China' plant.	Leaves	2·05 ,,
	Stems	0·28 ,,

From these figures it would seem that the leaves from the prunings, which are now thrown away or burnt, might possibly be used for the production of caffeine, but in all probability the cost of collection would be too high to admit of their use in a commercial undertaking.

Although coffee and several other plants contain appreciable quantities of caffeine, none of them appears to have been used in the manufacture of caffeine on a large scale, and it is not intended to discuss these sources in the present paper.

II. GENERAL METHODS OF EXTRACTION.

Although, as previously mentioned, the quantity of caffeine produced annually is by no means inconsiderable, there appears to be no adequate account of the process of manufacture. It is usually stated that an aqueous solution is prepared by digesting tea with hot water, and that this solution is treated with lime or lead salts or both, filtered and evaporated until the caffeine separates, or alternatively is evaporated with lead oxide to dryness and extracted with alcohol.

Between 1907 and 1910 numerous patents were taken out for extracting caffeine from coffee and simultaneously producing a caffeinless coffee. According to these, the caffeine was removed by extraction with aqueous alkali or sodium salicylate, or with volatile solvents such as alcohol, benzene, chloroform or ethyl acetate, but none of these processes appears to have developed commercially to any extent.

During the war, the manufacture of caffeine was started in Japan and several processes were patented. According to Japanese Patent 31014, tea dust is heated in an iron pan until the caffeine sublimes; Japanese Patent 31394 contains claims for the charring of waste tea and distillation of the caffeine with superheated steam. H. Hakucho[1] treats an aqueous extract with sulphur dioxide, adds excess of slaked lime, evaporates to dryness and extracts with benzene, while N. Suzuki[2] treats the aqueous extract with ferric sulphate and passes air to oxidise tannins, basic lead acetate is then added, the solution evaporated to dryness and the caffeine removed by sublimation.

Small quantities of caffeine have also recently been made in India and Ceylon by extracting tea fluff with kerosine oil at 160° or even at higher temperatures.

A. J. Ewins writing in *Thorpe's Dictionary of Applied Chemistry* (Revised Edition 1921, article 'caffeine') gives the most reliable description so far published of the process. He states that tea dust or damaged tea is mixed with 10 per cent. of slaked lime and extracted with boiling water or hot alcohol, and the extract after removal of the solvent treated with litharge or lead acetate. Alternatively the mixture of tea and lime is extracted with benzene and the caffeine recovered from the extract, after removal of the solvent, by means of hot water.

In considering the extraction of caffeine from tea fluff, due attention must be paid to the following facts :—

(1) Caffeine is not entirely present in the raw material as such, but is mainly combined with tannic acid; (2) caffeine is slowly decomposed when warmed with certain alkalis; and (3) tea fluff exerts a most powerful adsorption effect which greatly increases the difficulty of extraction.

It is also necessary to examine the solubility of caffeine in various solvents and the effect of these solvents on the other constituents of the fluff, while from the commercial point of view the relative costs of the different processes must be compared.

Our object has been to make a study of these factors and to obtain a few quantitative results indicating the relative efficiency of the various processes.

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[1] J. Pat. 32780.

[2] J. Pat. 31489.

III. METHODS OF ANALYSIS.

For the analysis of tea fluff, Allen's modification of Stahlschmidt's method was used, but it was found more convenient to weigh the solutions instead of measuring them, and the extraction was only carried out for an hour and a half as preliminary experiments proved that this was sufficient to remove practically all the caffeine. Details are as follows:—

Ten grams of fluff were gently boiled with 600 cc. of water in a covered beaker for 1·5 hours. The weight of solution, which evaporated slightly during the boiling, was made up to 607 grams, 7 grams being the approximate weight of the insoluble matter, and the whole strained through muslin. 500 grams of the filtrate were taken, 4 grams of solid lead acetate and 1 gram of litharge added, and the whole well stirred and boiled for about ten minutes until the weight reached 502 grams (2 grams insoluble matter). The solution was covered and the precipitate after settling filtered off. 400 grams of filtrate were evaporated to about 100 cc. on the water bath, the lead removed by the addition of a slight excess of sulphuric acid and the lead sulphate filtered off after continuing the concentration to about 25 cc. The precipitate was washed with about 5 cc. of water and the solution extracted four times with 10 cc. of chloroform. The filtration immediately before extraction prevented the formation of a middle emulsified layer and considerably facilitated the extraction. The chloroform was distilled off in a tared flask and the caffeine weighed. The caffeine obtained was almost white and check analyses by Kjeldahl's method showed the purity to be about 96 per cent.

In the case of tea juice, 50 cc. of juice were made up to 500 grams with water and treated with lead acetate and litharge as above.

Extracts made with volatile solvents were evaporated to dryness and extracted with boiling water. If the aqueous solution was not clear a few drops of basic lead acetate solution were added, the lead removed, the solution evaporated and the caffeine extracted with chloroform.

IV. EXTRACTION WITH WATER.

A series of experiments was carried out in which the tea fluff was extracted with water, and tannins and colouring matters removed with lead compounds or lime. Two outstanding facts were at once observed. Firstly, that in spite of the great solubility of caffeine in hot water it is not at all easy to extract it completely even in presence of alkalis, and secondly, that a considerable quantity of sugary matter is extracted with the caffeine and is not precipitated by lead acetate. On evaporation this material darkens, discolours the caffeine and makes it difficult to obtain the whole of it by crystallisation. A further difficulty is met with in the great volume of the precipitate produced by lead acetate: this precludes the use of very concentrated extracts, and is liable to engender losses due to incomplete washing.

Although statements have appeared which indicate that lime alone is sufficient to precipitate foreign matter and allow the caffeine to be crystallized from aqueous extracts, this is not the case. A solution so treated is deep brown in colour and it would be a matter of great difficulty to recover the caffeine by crystallisation alone. Lime may, however, conveniently be used to precipitate some of the soluble matter and effect an economy of lead salts. Table III shows the result of adding lime to the fluff before extraction. 50 grams of fluff were mixed with varying amounts of lime, boiled with 500 grams of water for half an hour, the solution strained through fine muslin and the residue well pressed, boiled with a second 500 grams of water and again pressed. The combined extracts were boiled and a 10 per cent soluion of basic lead acetate added gradually until no further precipitate was produced. The results are calculated to grams of pure calcium oxide and grams of basic lead acetate Pb $(C_2H_3O_2)_2$, PbO per 100 grams of tea fluff.

TABLE III.

Quantity of basic lead acetate required for precipitation of tea fluff extracts treated with lime.

Grams CaO per 100 grams fluff.	Grams lead acetate per 100 grams of fluff a
0	9·8
2	6·8
4	4·5
8	4·1
12	3·9

The fluff used in these experiments was from Travancore. Another sample from Assam when mixed with 8 per cent. of lime required 3·1 grams of basic lead acetate.

It is thus evident that rather more than half the amount of lead acetate required for precipitation may be saved by the addition of lime, and that a convenient quantity of the latter reagent to add is about 5 per cent. calcium oxide on the weight of the fluff.

A few preliminary extraction experiments were sufficient to show that, in spite of the high solubility of caffeine in hot water and the fine state of division of the tea fluff, solution is by no means readily effected. In order to obtain a high percentage extraction it is necessary to digest the material for several hours, but even then, with comparatively concentrated solutions the fluff retains a considerable proportion of the caffeine. It is desirable, before evaporation, to bring the solution of caffeine up to the highest possible concentration and hence to use as little water as possible for the extraction, but the problem is complicated by the retention of caffeine by the fluff and in practice only very dilute solutions can be obtained. The addition of four parts of water to one part of tea fluff produces a stiff mass, and it is desirable to use at least 5 parts of water to enable the mixture to be stirred during digestion. On centrifuging or pressing the mass, the residue retains a weight of extract at least equal to that of the dry fluff and in most cases about 1·4 times this weight, so that with 5 parts of water to 1 of fluff only about 70 per cent. of the extract is obtained in the first operation. The concentration of caffeine in the solution is only 0·3 per cent., or at most 0·4 per cent., if a high grade fluff is used and lime is added before extraction. If this solution is boiled with one-fifth of its weight of fresh fluff, the concentration of caffeine is not doubled, as might be expected, but only rises by about 70 per cent. On repeating the operation the increase in concentration is proportionately less on each extraction, until finally it is found that a solution which contains about 1·3 per cent of caffeine is in equilibrium with the fluff and will extract no more alkaloid.

Not only is it very difficult actually to prepare concentrated aqueous solutions of caffeine from the fluff, but it is also inadvisable to attempt to work with such solutions, as the voluminous nature of the precipitate obtained by the addition of basic lead acetate renders filtration and washing very difficult. Even with a concentration of caffeine of only 0.3 per cent. and preliminary treatment with lime the solution containing the lead precipitate is almost of pasty consistency. If precipitated under proper conditions however, the precipitate is more readily filtered and washed in a filter press than might be expected, but it would not be possible appreciably to increase the concentration; and the treatment, by this method, of solutions containing 1 per cent. of caffeine would be exceedingly difficult.

Table IV contains some figures illustrating the extent to which caffeine is extracted from tea fluff by water. The experiments to which they refer were made by digesting the fluff, either alone or mixed with lime, with water in a steam heated pan, keeping the mixture just boiling and stirring at intervals. The mass was then removed and centrifuged or placed in a bag and pressed in a screw press until as much liquor as possible was removed. The extract and residue were weighed and the percentage of caffeine in the former estimated. Preliminary experiments showed that under similar conditions the total dry insoluble matter after extraction was nearly 70 per cent. on the weight of the original fluff when no lime was added, and 85 per cent. when lime was present. From these figures it is possible to calculate with sufficient accuracy the weight of the total solution and the quantity of caffeine in it. The difference between this and the amount originally in the fluff gives the quantity not extracted. In the first group of experiments fresh fluff was treated and in the second the residue from the first extraction was used. The fluff in the larger scale experiments was all from the same sample and contained 2·23 per cent. of caffeine. The lime used was of rather poor quality and contained only 40 per cent of calcium oxide.

TABLE IV.

Extraction of Caffeine from Tea-fluff by water.

No.	Weight of fluff in lbs.	Weight of lime in lbs.	Ratio water-fluff	Time of extraction in hours	Weight of extract in lbs.	Weight of wet residue in lbs.	Concentration of caffeine in extract	Percentage of total caffeine in total solution
1_1	0·44	0·0	9·7 : 1	0·5	3·68	1·03	0·185	82
2_1	10	0·8	5·5 : 1	1	43·5	23·5	0·269	68
A_1	30	1·8	5·1 : 1	1	109·5	77·0	0·310	72
B_1	30	1·8	4·8 : 1	1	118·0	61·0	0·364	66
D	30	2·1	5·3 : 1	8	120·0	75·0	0·335	81
E_1	10	0·3	7·2 : 1	2	63·0	19·5	0·217	72
F_1	15	0·3	7·8 : 1	2	116·0	28·0	0·226	82
G	5	0·0	8·5 : 1	18	37·8	9·5	0·175	69
1_2	0·44	0·0	6·5 : 1	0·5	2·04	1·15	0·095	89
2_2	10	0·8	5·0 : 1	1	37·0	23·5	0·156	73
2_3	10	0·8	5·3 : 1	1	42·5	20·5	0·076	78
A_2	30	1·8	4·7 : 1	1	100·5	70·5	0·150	67

During the experiments a considerable amount of evaporation took place and the figures for the ratio water : fluff are calculated from the weight of water at the end of the extraction. In Experiment B_1 the fluff was treated with the solution obtained in Experiment A_2 (100 lbs.) in addition to 50 lbs. of water. This, together with the low proportion of water, accounts for the high concentration of caffeine in the solution, but the amount of caffeine in solution is only 66 per cent. of the total. It may also be calculated that only 58 per cent. of the caffeine in the fluff dissolved on extraction.

In Experiment E_1 the centrifuged residue was washed with 6 lbs. of hot water, but this had little or no effect on the amount of caffeine dissolved.

In experiment G boiling was continued without lime for 18 hours, the residue dried and the caffeine in it estimated. The dry residue weighed 3·5 lbs. and contained 0·033 lb. of caffeine. Of this 0·010 lb. came from the evaporated solution while the separated extract contained 0·066 lb., so that the total extract contained 0·076 lb. and the fluff 0·023. The total caffeine originally present was 0·112 lb., so that 0·013 lb. or 11·6 per cent. was lost by decomposition during the prolonged boiling.

The experiments show that—

(*a*) on boiling tea fluff with water with or without the addition of lime only about 70-80 per cent. of the caffeine is dissolved,

(*b*) if attempts are made to raise the concentration of the solution much above 0·3 per cent. by boiling a weak solution with fresh fluff, a still smaller proportion of caffeine dissolves,

(*c*) boiling for several hours is advisable,

(*d*) a larger proportion of caffeine is dissolved by more dilute solutions as might be expected.

In the second group of experiments with extracted fluff and fresh water similar results were obtained but the figures for the percentage of caffeine dissolved are probably low as no account is taken of slight mechanical loss or the decomposition of caffeine during extraction. Experiment 2_3 gives the results of a third extraction of the material used in Experiments 2_1 and 2_2.

The solutions obtained in these experiments were treated with lead compounds in order to test this method of removing impurities and obtaining the caffeine by crystallisation. A complete series of experiments could not be conveniently carried out owing to the large number of possible variations of the method, but the following results indicate the nature of the process.

1. Solutions A_1 and B_1 (103 kg.) were mixed, boiled, and 1 ko. of litharge ground to a paste with water added; very little precipitate was produced and 150 grams of lead acetate in solution was then added and the whole boiled for some time. A bulky precipitate was produced which was filtered and washed on a filter press. The solution and washings, which were clear but sherry coloured, were boiled down in a steam jacketted pan to about two litres and on cooling 77 grams of dark brown caffeine crystals separated. Calcium salts

(*c*) Two litres of solution were treated as above with 80 cc. of the basic lead acetate solution and after filtration and concentration to 670 cc. divided into three portions. The first was evaporated under reduced pressure to 30 cc., the second was boiled just to dryness over a small flame, and the third was taken to dryness on a water-bath. The first solution, which solidified on cooling, was much paler in colour than the other two between which there was little difference.

Eighteen litres of the solution containing 39·6 grams of caffeine were then boiled and treated with 360 cc. of the basic lead acetate solution as in (*b*). The precipitate formed settled well and was readily filtered. The solution was boiled down to 600 cc. in a steam pan and the solid which separated on cooling recrystallised from hot water. The solution was then further concentrated and the process repeated. The following quantities were obtained :—

Volume 600 cc. total crystals = 11 grams caffeine = 6·0 grams.
,, 400 cc. ,, ,, 12 ,, ,, 4·5 ,,
,, 280 cc. ,, ,, 13 ,, ,, 4·1 ,,

making a total of 14·6 grams of caffeine, or only 37 per cent. of that originally present. A certain additional quantity could have been recovered from the mother liquors, but it is evident that the loss is very high and it would seem that the disappearance of caffeine takes place either by volatilisation or decomposition, during the process of boiling down the solution.

3. Solution F_1 (*a*) (21·6 kg. containing 49 grams of caffeine), which had been prepared without the addition of lime, required considerably more basic lead acetate solution than was used in the last experiment. After addition of 8·6 cc. of the same basic lead acetate solution to 100 cc. a precipitate was still produced, but it was white. The whole solution was boiled with two litres of the lead acetate solution or 9·2 cc. per 100 cc. Part of the subsequent filtration was done cold, and, probably owing to this, the resulting solution, which weighed 20·5 kg., contained only 38 grams of caffeine.

This solution contained lead, and gave no precipitate with normal lead acetate, but gave a yellow precipitate with alkalis and basic lead acetate. Consequently it was cautiously evaporated to about 10 litres and caustic soda followed by ammonia added until no further precipitate was produced. It was then filtered and concentrated to 930 cc. in a steam pan and slowly evaporated to 480 cc. in a basin. When cool, 31 grams of solid separated, yielding 14·5 grams of caffeine on recrystallisation. On concentrating to 260 cc. 3·5 grams more of caffeine was obtained, making 18 grams in all or 47 per cent. of the amount originally in the clarified solution. This is a better result than in the previous experiment, but the loss is still high. A separate portion of 960 grams of the original clear solution, on very slow evaporation in a porcelain basin to 80 cc., gave practically the theoretical yield of caffeine, showing that the losses are due to the process of boiling down.

4. Solution $F_1(b)$, which was similar to $F_1(a)$, but prepared with the addition of lime, was clarified as before with basic lead acetate solution, and 14 litres containing 39·6 grams of caffeine were just acidified with hydrochloric acid and evaporated under reduced pressure in a film evaporator[1] to 1 litre. 15 grams of fairly clean crystals were deposited on cooling and yielded 12·4 grams of white caffeine on recrystallisation. The mother liquor was put through the evaporator a second time and concentrated to 250 cc. This solution set on cooling and gave 25 grams of a white solid containing 15·6 grams of caffeine. The total yield was thus 28 grams or 71 per cent., a very great improvement.

A few experiments were carried out to try the applicability of the method to the tea juice which is obtained when rolling the leaf in wet weather, using a sample from Assam containing 0·5 per cent. of caffeine. The juice gave a large precipitate with milk of lime or basic lead acetate, and on evaporation to one-tenth of its volume formed a viscous mass which it was not easy to dry. Assuming, however, that the total solids were 8 per cent., the ratio of total soluble matter to caffeine is 16 to 1, whereas in tea fluff the ratio is only about 8 to 1, consequently it is evident that larger quantities of reagents will be required per lb. of caffeine for the juice than for fluff.

The following experiments afford a certain amount of information as to the quantities of reagents required and the yields obtained :—

1. Two litres of juice containing 5 grams of caffeine were treated with a quantity of slaked lime corresponding with 45 grams of calcium oxide and gave a copious precipitate, but on filtration and concentration under reduced pressure the solution became thick and no caffeine separated.

2. Two litres of juice were treated with lime as above and 200cc. of basic lead acetate solution containing 30 grams of solid, added. The filtrate, after acidifying, was concentrated under reduced pressure to 250 cc., but only a very few crystals of caffeine separated on cooling.

3. Two litres of juice were treated with lime as in the last experiment and then with 400 cc. of the basic lead acetate solution.

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[1] cf. this Journal, 1919, **2**, 209.

After filtration and removal of the lead the solution was acidified and concentrated under reduced pressure. The concentrated solution was much clearer and gave 5·7 grams of caffeine while the mother liquor was analysed and found to contain 1·66 grams making a total of 11·88 grams or 62 per cent. of the caffeine originally present. It is thus seen that even in a simple operation of this nature the loss of caffeine may be very high.

4. An experiment similar to the last was carried out with ten litres of juice and five times the quantities of other reagents. 95 per cent. of the clarified solution was concentrated under reduced pressure and gave 23·4 grams of caffeine crystals, 3·8 grams were found in the mother liquor while 6·0 grams remained in the precipitates even after washing, in all 65 per cent. of what was originally present. The remaining 5 per cent. of solution was boiled down in a porcelain dish and gave only 60 per cent. of the original caffeine.

5. 500 cc. of juice was treated with 10 grams of magnesia and 135 cc. of the basic lead acetate solution. The clear solution after concentration on the water bath gave 1·19 grams of crystals and the mother liquor and precipitates contained 0·96 grams of caffeine, together 80 per cent. of the caffeine originally present, a considerable improvement on the experiments with lime.

From these examples it will be seen that this method of extraction presents several disadvantages. The occlusive power of the tea fluff complicates the process of extraction, and the great volume of precipitate obtained with lead salts makes it impracticable to raise the concentration of caffeine in solution much above 0·5 per cent. This means that about 200 lbs. of water has to be evaporated for every 1 lb. of caffeine produced. The quantity of basic lead acetate required even when lime is used is considerable, about 2 lbs. per 1 lb. of caffeine and forms a very appreciable item of expense. Although it is possible to recover a large proportion of the lead oxide, it is doubtful if it would pay to do so except in a very large factory. Finally it appears essential to carry out the evaporation under reduced pressure, while throughout the whole series of operations the very greatest care must be exercised to prevent volatilisation or decomposition of caffeine.

Although this method of extraction or some modification of it was formerly used almost exclusively, it is not surprising to find that it has now been largely, if not entirely, supplanted by more modern processes. Such processes involve the use of volatile solvents, and the following experiments were carried out with a view to examining certain of the details connected with them.

V. THE SOLUBILITY OF CAFFEINE.

In considering any process for the extraction of caffeine by means of volatile solvents it is necessary to know the solubility of caffeine in these solvents at different temperatures. A number of figures are available, the most important being those of A. Commaille, Göckel and A. Seidell.[1] These are given in Table V.

TABLE V.

Solubility of caffeine in grams per 100 grams of solution.

Solvent		Temperature in degrees cent.	Solubility	Temperature in degrees cent.	Solubility
Water	(*a*)[1]	15-17	1·3	65	31
	(*d*)	25	2·24	80	16
Absolute alcohol	(*a*)	15-17	0·60	78	3·0
	(*d*)	25	1·85	60	5·5
Rectified spirit	(*a*)	15-17	2·2	...	...
Amyl alcohol	(*a*)	25	0·49	...	...
Dry ether	(*a*)	15-17	0·04	35	0·36
	(*b*)	18	0·12	35	0·29
	(*d*)	25	0·27	...	...
Acetic acid	(*c*)	21.5	2·44	...	...
Amyl acetate	(*c*)	30	0.72	...	...
Petroleum spirit	(*a*)	15-17	0·03	...	...
Acetone	(*c*)	30-31	2·18	...	...
Chloroform	(*a*)	15-17	11·5	61	16·0
	(*b*)	18	10·5	61	13·5
	(*d*)	25	11·1	...	...
Carbon tetrachloride	(*b*)	18	0·09	77	0·70
Carbon disulphide	(*a*)	15-17	0·06	46	0·45
Benzene	(*b*)	18	0·90	80	5·0
	(*c*)	30	1·22	...	...
Toluene	(*c*)	25	0·57	...	...
Xylene	(*c*)	32·5	1·11	...	...
Benzaldehyde	(*c*)	30-31	11·62	...	...
Aniline	(*c*)	30-31	22·89	...	...

Commaille's figures (*a*) refer to the anhydrous substance.

The solubility of caffeine in aqueous solutions is very largely influenced by the presence of salts. S. B. Schryver[2] has made a number of determinations of the solubility of caffeine in normal salt solutions at 23·7° C. and the following are some of his results in grams of anhydrous caffeine per 100 cc. of solution :

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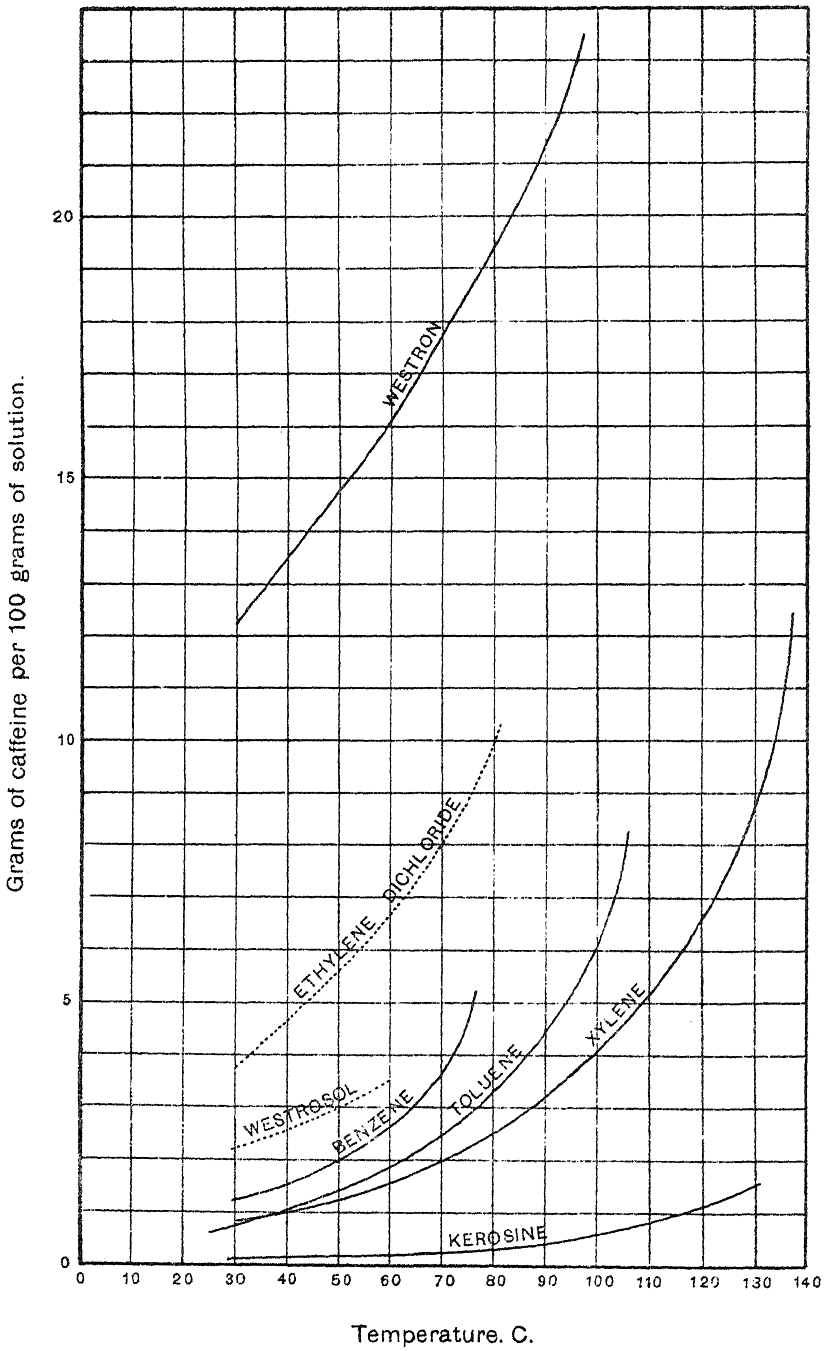
[1] A. Commaille *Compt. rend.*, 1875, **81**, 817 (*a*) ; Göckel *Chem. Zent.*, 1897, **2**, 401 (*b*) ; A. Seidell *J. Amer. Chem. Soc.*, 1907, **29**, 1091 (*c*) ; and the *United States Pharmacopœia* 9th Edn., 1916 (*d*).

[2] *Proc. Roy. Soc.*, B. 1910, **83**, 96.

Figure I

Solubility of caffeine at different temperatures.



Water 1·91, sodium chloride 1·27, sodium acetate 0·95, sodium citrate 0·80, sodium sulphocyanate 5·59, sodium benzoate 15·06, and sodium salicylate 23·05.

As not many figures are available for the solubility in hot solutions, we have made additional determinations with the following solvents :—benzene, toluene, xylene, ethylene dichloride, trichlorethylene (' westrosol '), acetylene tetrachloride (' westron '), kerosene oil and ' hydrocarbon ' B.P. 70°-110°, the latter being the liquid condensed on compressing oil gas and containing about 33 per cent. of benzene and toluene.[1] The three solvents first mentioned were commercial ' pure ' samples and were not dried. The caffeine used was anhydrous. The temperature during the period of solution was kept constant to within one degree in a thermostat fitted with a shaker. A weighed quantity of the clear saturated solution was taken in each case, the solvent distilled or evaporated off on the water bath, and the residual caffeine weighed. In the case of kerosene oil, the solution was first extracted with chloroform.

The results obtained are shown below in Table VI and represent grams of anhydrous caffeine per 100 grams of solution and a series of curves showing the solubility at different temperatures is given in Fig. I.

TABLE VI.

Solubility of anhydrous caffeine in various solvents.

Solvent	Temperature in degrees centigrade					
	30	60	80	97	110	130
Benzene	1·20	2·60	5·18 (77°)	...	...	...
Toluene	0·72	1·80	3·27	...	8·2 (107°)	...
Xylene	0·80	1·53	...	3·93	5·1	12·4 (137°)
' Hydrocarbon ' B.P. 70°-120°	0·80	2·05	...	...	...	...
Ethylene dichloride ...	3·83	...	10·3	...	...	...
Trichlorethylene B.P. 83°-110°	2·28	3·57	...	...	...	...
Acetylene tetrachloride 135°-145°	12·25	16·12	...	23·5	...	...
Kerosene oil D. 0·802 ...	0·04	0·14	...	0·53	...	1·63

Examination of Tables V and VI will show that, of the solvents in which caffeine is appreciably soluble, water, alcohol and the hydrocarbons have a very high temperature coefficient of solubility, and in

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[1] Cf. this Journal, 1918, 2, 73.

addition, the solubility at ordinary temperatures is very low. Consequently, it is essential when using them to keep the temperature high. Kerosene oil, for example, could only be used at inconveniently high temperatures. Of the benzene hydrocarbons, at any temperature above 40° C., the order of solubility is benzene, toluene, xylene, benzene having the greatest solvent power; but at their boiling points, the order is reversed. Hydrocarbon is intermediate between benzene and toluene.

Another class of solvents comprises the chlorinated derivatives of methane and ethane, and in these caffeine is readily soluble at ordinary temperatures, but the ratio of the solubilities at 100° and 25° is lower than that for the benzenoid hydrocarbons. Carbon tetrachloride forms a remarkable exception. It is not clear to what class of solvents benzaldehyde and aniline belong as the solubilities have not been determined at higher temperatures.

Of these solvents, the only three at present available in India in quantity are alcohol, petrol and kerosene oil. The use of alcohol has certain disadvantages, not the least of which are the restrictions placed upon its use by the Revenue Department. The solubility of caffeine in petrol is too low to make it of much use as a solvent and the same holds good with regard to kerosene oil unless the temperature is raised very considerably, and then decomposition of the caffeine results. A certain quantity of 'hydrocarbon' is to be had, but the experiments which follow show that this solvent is by no means ideal. The organic chlorine compounds are not made and are not likely to be made in India for many years and their high cost, combined with the heavy freight, would render the use of the imported substances out of the question. The only possible commercial solvents appear to be benzene or toluene. These will probably be recovered from coke oven plants in the near future so that importation would be unnecessary. Most of the following experiments were carried out with toluene, as the solubility of caffeine at the boiling point is somewhat higher than in the case of benzene, and owing to the higher boiling point condensation is simplified. At the same time, however, there is the disadvantage that under certain conditions the amount of decomposition is greater.

VI. DISTRIBUTION OF CAFFEINE BETWEEN TEA FLUFF AND SOLVENTS.

Owing to the adsorbtive power of tea fluff already mentioned, (p. 183) in the case of water, it was anticipated that the extraction of caffeine by means of a solvent in which it was far less soluble might prove a matter of considerable difficulty. To test this point the following experiments were carried out. Ten grams of tea fluff were placed in a flask with a known weight of solvent and digested with frequent shaking for a certain period in boiling water. A reflux condenser was fitted and the whole flask weighed at the beginning and the end of the digestion to ensure that no solvent had escaped. A known weight of the clear hot solution was then poured into a distilling flask and the solvent removed. The total weight of caffeine and green resinous matter was determined and the former dissolved in warm water. Filtration gave a clear solution from which very nearly pure caffeine could be obtained by evaporation. From the weight of this, the total caffeine present in solution could be calculated. The results are shown in Table VII. Duplicate experiments gave concordant results.

TABLE VII.

Distribution of caffeine between tea fluff and various solvents.

No. of Experiment	Weight of fluff in grams	Solvent	Weight of solvent in grams	Time of digestion in hours	Percentage of total caffeine dissolved by solvent	Remarks
1	10	Toluene	20	1	24	
2	10	,,	20	3	32	
3	10	,,	40	3	38	
4	10	,,	80	3	48	
5	10	Kerosene oil	80	3	15	
6	10	Toluene	80	3	49	4 cc. water added.
7	10	,,	80	3	8	4 cc. water added to fluff and dried at 100° before extraction.
10	10	,,	80	3	7·4	30 cc. of water added and the whole dried.
8	10	,,	20	3	23	0·45 g. CaO added and whole dried before extraction.
11	10	,,	80	3	45	0·9 g. CaO added.
9	10	,,	80	3	62	0·9 g. CaO and 4 cc. water added.
12	10	,,	80	2	74	0·9 g. CaO and 60 cc. water added. Evaporated until moisture content 33 per cent. and then extracted.
13	150	Water	750	2	66	
17	150	,,	750	2	78	17 g. CaO added.
14	60	Tea juice	300	2	48	Solvent contained 0·318 per cent. caffeine.
18	60	,,	300	2	56	7 g. CaO added.
15	40	2 per cent. caffeine solution.	200	2	−254	Fluff partially extracted. Contained 1·76 per cent. caffeine. It absorbed from the solution 2·54 times the weight of caffeine originally present.
16	20	,,	100	2	−79	Similar experiment with fresh fluff.

Experiments 1 and 2 show that although the extraction proceeds slowly, the rate of solution diminishes considerably after the first hour and equilibrium is probably almost complete at the end of three hours. Consequently the other experiments were carried out for three hours, and the results should be comparable. Experiments 2, 3 and 4 show that doubling the quantity of solvent does not by any means double the quantity of caffeine dissolved; the ratio of the concentration of caffeine in the solvent to the concentration in the solid, viz. 0·24 : 1, 0·16 : 1 and 0·11 : 1 by weight in the three cases, indicates that the solid retains the caffeine most tenaciously. To some extent this may be due to the existence of the caffeine as a compound with tannin, but adsorption undoubtedly plays a considerable part.

In Experiments 8, 11, 9, and 12 sufficient slaked lime was added to decompose any caffeine tannate, but although the quantity of caffeine dissolved increased somewhat, by no means the whole amount went into solution.

The effect of water is very marked. If the fluff is moistened with water and then dried before extraction, very little caffeine is dissolved (Experiments 7 and 10). It was anticipated that the water would dissolve the caffeine and on drying would deposit it on the outside of the fluff particles in an easily soluble form, but this does not appear to be the case. If lime is added and the fluff dried a slightly larger quantity of caffeine is dissolved but the amount is still small (Experiment 8). The addition of water or lime alone to the original fluff does not appreciably affect the extraction (Experiments 4, 6 and 11), but the addition of both these substances largely increases the solubility (Experiments 9 and 12). The best result was obtained by adding sufficient water to make a paste and evaporating down until the moisture content was about 33 per cent., and it is remarkable that so much caffeine should be obtained in the toluene solution in the presence of about 5 grams of water in which caffeine is about five times as soluble as it is in toluene, for, as shown by Experiment 17, much of the caffeine must remain undissolved in either solvent.

With regard to other solvents, it will be seen that kerosene oil extracts far less caffeine than toluene under similar conditions, as might be expected from the relative solubilities. Five parts of water extract a large proportion of the caffeine (Experiment 13) and this is increased by the addition of lime (Experiment 17). On the other hand, if tea juice containing caffeine is used as solvent, a much lower percentage of caffeine is extracted from the fluff (Experiments 14 and 18). If a still more concentrated solution of caffeine is used for extraction, the fluff actually absorbs caffeine from the solution, and this is particularly marked in the case of the partially extracted fluff used in Experiment 15, in which the percentage of caffeine in the fluff rose from 1·76 to 6·41 while that of the solution fell from 2·00 to 1·07. In the case of fresh fluff (Experiment 16) the absorption was not so great, but it was still very marked. The percentage of caffeine in the fluff rose to 4·3 and that in the solution diminished to 1·6 showing that it is impossible to obtain an aqueous solution containing 1·6 per cent. of caffeine from ordinary fluff containing about 3 per cent.

VII. THE DECOMPOSITION OF CAFFEINE BY ALKALIS.

As the experiments already described proved the necessity of alkalis to decompose the caffeine tannate before extraction with a solvent such as toluene, a series of experiments was carried out in order to ascertain the extent to which caffeine itself is decomposed by such treatment. It has been stated by A. H. Allen[1] that lime decomposes caffeine while magnesia does not, and consequently the effect of both these alkalis was studied. Two different methods were adopted. In the first a mixture of tea juice and tea fluff was made in a long-necked flask and the alkali added. The whole was well shaken, immersed in a boiling water or an oil bath for a considerable time and shaken at intervals. Water was added from time to time to replace any lost by evaporation, and at the end of the experiment the mixture was removed and the caffeine content determined. As the amount originally present in the fluff and juice was known the loss was readily ascertained. As a modification some experiments were carried out in a basin or large crucible placed in an oil bath, to imitate to some extent the process used later on a larger scale of boiling down the mixture in a steam-heated pan.

In the second series of experiments a known weight of pure anhydrous caffeine was treated with a little water and alkali, digested under a reflux condenser with toluene or hydrocarbon and the caffeine estimated at the end of the process.

The results are shown in Table VIII together with some figures obtained when preparing larger mixtures for extraction purposes. The small scale experiments were done in duplicate and the results agreed to within 1 per cent. of the total caffeine. In the table only mean values are given.

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[1] *Pharm. J.*, 1892, iii, 23, 215.

TABLE VIII.

Decomposition of caffeine by alkalis.

No.	Fluff	Juice	Lime	Magnesia	Time in hours	Temperature	Percentage Decomposition
1	5 grams	20 cc.	1·2 grams	...	20	90°	19·0
2	5 ,,	20	...	0·8 grams	20	90°	0·0
3	5 ,,	30	0·75	...	20	90°	0·6
4	5 ,,	30	0·7	0·25	20	90°	1·9
5	10 ,,	60	2·5	...	20	97°	13·8
6	10 ,,	60	2·5	...	10	97°	7·8
7	5 ,,	30	1·25	...	10	90-95°	3·4
8	5 ,,	30	1·25	...	10	90-95°	1·2
9	5 ,,	30	1·25	...	10	74-101°	1·9
10	45·5 kg.	136 kg.	4 kg.	3·8 kg.	...	...	5
11	45·5 ,,	136 ,,	...	7·6 ,,	...	...	4
12	80·0 ,,	240[1] ,,	3·5 kg.	3·5 ,,	...	...	4·6[2]
	Caffeine	Water		Na_2CO_3			
13	2 grams	2 cc.	0·7	...	20	72°	2·7
14	2 ,,	2 ,,	0·7	...	30	107°	19·5
15	2 ,,	2 ,,	...	1·35	30	107°	4·5

Experiments 1 to 4 were carried out in a flask under comparable conditions. It will be seen that excess of lime produces considerable decomposition, but the equivalent quantity of magnesia is without effect. Lime not in excess does not appreciably decompose the caffeine, even when magnesia is added to it so that the total alkali is in excess. Numbers 5 and 6 were done in an oil bath heated to 130° and it will be seen that the decomposition is roughly proportional to the time, but it is not quite clear why the decomposition should have been less than in No. 1 unless it is owing to the lower concentration of lime. Experiments 7, 8 and 9 were carried out in open dishes or crucibles in an oil bath. As evaporation was very rapid the temperature was irregular owing to frequent additions of water. In No. 9 no water was added and the temperature fell considerably as soon as the evolution of steam had ceased. In all the experiments under these conditions the decomposition, even with excess of lime, is slight.

The large scale experiments, Nos. 10, 11 and 12, were carried out by mixing tea fluff with concentrated juice and water to simulate natural juice, or in some cases with water alone and the mixture boiled down in a steam pan until water would not drain from the semi-solid mass. Drying was continued on an iron plate, heated by exhaust steam, until the moisture content reached about 30 per cent. The process occupied about three hours, and it will be seen that, even though an excess of lime was avoided, an appreciable loss of caffeine took place.

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[1] Water.

[2] Mean of 4·7, 5·0, 4·2.

The results of Experiments 13 and 14 were obtained by boiling moist caffeine, lime and water with 'hydrocarbon' and toluene respectively. At the higher temperature the decomposition is very considerable and points to the inadvisability of carrying out prolonged extractions with toluene in presence of excess of lime. On the other hand, if the lime is replaced by sodium carbonate, as in the last experiment, much less decomposition occurs.

VIII. EXTRACTION EXPERIMENTS.

A number of small scale extraction experiments were carried out to test the effect of varying the conditions on the rate of extraction. 100 grams of fluff or 50 grams of fluff mixed with 300 cc. of juice and concentrated, were used as the source of caffeine. The volume in each case was approximately the same. In most cases alkali was added and the whole introduced into a Soxhlet extractor. The solvent was boiled and allowed to fill the extraction vessel and syphon over six times. The receiver was then changed and the extraction continued for six more syphonings. As far as possible the rate of boiling was regulated so that each filling and emptying of the extractor took the same time in all experiments. The approximate volume of liquid syphoning over each time was 33 cc. and the volume retained by the fluff 140 cc., so that assuming the fresh solvent did not mix with what was already in the fluff the solvent was completely renewed every six syphonings. In practice the renewals were rather less than this. In Experiments 15 and 16 eight syphonings were carried out in each extraction and in Experiments 28 to 32 three extractions each of six syphonings were made. When the extractions were complete the solvent was distilled off and the total extract weighed. The caffeine was removed by extraction with warm water, filtration, and, if necessary, by solution in chloroform. It was usually only lightly coloured and practically pure.

The results obtained are recorded in Table IX.

These experiments lead to a number of conclusions.

In the first place it is evident that caffeine is not at all easily extracted from tea fluff in its normal condition, i.e. with about 10 per cent. of moisture. The result of Experiment 3 is even lower than would be expected from the distribution experiments in Table VII, p. 193. This is probably due to the temperature in the Soxhlet being rather lower than in a flask immersed in boiling water.

TABLE IX.

Results of small scale extraction experiments.

Experiment No.	Wt. of fluff grams	Juice grams	CaO grams	MgO grams	Water grams	Per cent of moisture in charge	Total time of extraction in hours	Ratio of green colouring matter extracted to caffeine in charge	CAFFEINE EXTRACTED		Total	Solvent	Remarks
									first extraction	second extraction			
3	100	...	...	...	...	10	1·2	0·44	8·2	3·4	11·6	Toluene	...
4	100	...	...	...	10	18	0·5	0·53	13·0	...	13·0	,,	Only one extraction.
20	100	...	...	...	300	33	2·3	0·37	8·6	10·8	19·4	,,	...
5	100	...	17	...	10	15	1·5	0·32	4·6	11·2	15·8	,,	...
7	100	...	17	...	300	15	1·5	0·79	49·5	11·0	60·5	,,	...
21	100	...	17	...	52	33	1·3	0·29	38·9	38·5	77·4	,,	....
8	100	...	17	...	300	33	1·5	0·45	62·4	18·5	80·9	,,	...
6*a*	50	300	17	...	...	33	5·0	0·86	89·8	11·0	100·8	,,	Caffeine impure.
6*b*	50	300	17	...	...	33	4·3	0·48	71·7	12·3	84·0	,,	...
11	50	300	8·5	...	...	33	1·7	0·21	50·6	37·8	88·4	Hydrocarbon	...
12	50	300	10	...	...	33	1·2	0·25	64·9	17·2	82·1	,,	...
9	50	300	17	...	...	33	1·8	0·59	77·2	8·7	85·9	,,	...
13	50	300	8	2·5	...	33	2 1	0·41	73·7	8·8	82·5	,,	...
14	50	300	2	6·4	...	33	2·5	0·27	70·5	18·4	88·9	,,	...
15*a*	50	300	17	...	...	33	2·5	0·43	79·6	6·6	86·2	,,	8 syphonings per extraction.
15*b*	50	300	17	...	...	33	3·2	0·36	79·8	9·3	89·1	,,	,,
16*a*	50	300	8·5	4·3	...	33	2·5	0·81	75·9	5·5	81·4	,,	,,
16*b*	50	300	8·5	4·3	...	33	2·3	0·86	76·1	10·3	86·4	,,	,,
19	100	...	...	...	...	0	6·0	0·44	...	...	1·9	,,	About 35 syphonings.
1	20	...	2·7	...	10	35	7·0	...	...	...	45·0	Alcohol	...
2	20	...	...	...	...	28	7·0	...	40·0	1·4	41·4	,,	5 cc. conc. ammonia solution added.
18	50	...	8·5	...	...	0	9·0	...	...	...	83·0	,,	About 50 syphonings.
10	50	300	17	...	...	33	3·3	0·11	13·0	0·0	13·0	Petrol 100°–140°	...
22*a*	100	...	...	30	50*	33	2·3	0·33	68·5	23·8	92·3	Toluene	...
22*b*	100	...	...	30	50	33	2·7	0·34	64·1	24·0	88·1	,,	...
23*a*	100	...	...	30	50	25	1·8	0·41	46·6	30·3	76·9	,,	...
23*b*	100	...	...	30	50	25	1·5	0·43	54·1	24·8	78·9	,,	...
24*a*	100	...	...	30	50	20	1·3	0·36	41·7	30·5	72·2	,,	...
24*b*	100	...	...	30	50	20	1·3	0·37	54·2	20·3	74·5	,,	...
25	100	...	...	30	20	20	1·3	0·36	26·5	25·5	52·0	,,	...
26*a*	100	...	...	30	50	10	1·7	0·35	39·3	13·9	53·2	,,	...
26*b*	100	...	...	30	50	10	1·7	0·32	33·5	19·1	52 6	,,	...
27*a*	100	...	...	30	50	0	1·7	0·17	8·7	3·8	12·5	,,	...
27*b*	100	...	...	30	50	0	1·5	0·24	10·0	5·8	15·8	,,	...
28*a*	100	...	...	7·5	38·7	33	2·5	0·34	80·8	12·3	93·1	,,	18 syphonings. The figures for first extraction are for the first twelve syphonings.
28*b*	100	...	...	7·5	38·7	33	2·8	0·32	86·1	9·4	95·5	,,	
29*a*	100	...	...	7·5	22·5	25	3·0	0·35	77·8	13·1	90·9	,,	
29*b*	100	...	...	7·5	22·5	25	2·8	0·34	79·6	14·2	93·8	,,	
30*a*	100	...	...	7 5	300	33	3·5	0·35	85·0	9·6	94·6	,,	
30*b*	100	...	...	7·5	300	33	3·3	0·39	87·8	6·4	94·2	,,	
31*a*	100	...	...	5·0	37·5	33	2·8	0·45	72·3	19·4	91·7	,,	
31*b*	100	...	...	5·0	37·5	33	2·7	0·41	83·8	9·9	93·7	,,	
32	50	100	...	7·5	50	33	3·3	0·24	72·5	18·9	91·4	,,	

* From 22a to 32 this weight represent grams of anhydrous sodium carbonate.

When the tea fluff was completely dried and exhaustively extracted (Experiment 19) only 1·9 per cent. of caffeine was obtained. This quantity probably represents the free caffeine in the fluff, the remainder being combined with tannic or other acids. This experiment was carried out with hydrocarbon as solvent to avoid the possible decomposition of the caffeine by boiling toluene.

The addition of a small quantity of water to the fluff slightly increased the amount of caffeine extracted (Experiment 4) while the addition of a considerable quantity of water followed by evaporation to a 33 per cent. moisture content resulted in a further increase, but the amount extracted was still comparatively small, viz. 19·4 per cent. (Experiment 20). The addition of an excess of lime mixed with a little water, as in Experiment 5, had but little effect; in fact, the quantity of caffeine extracted in this experiment was only slightly greater than in Experiment 4 without lime, in spite of the time of extraction being three times as long. When, however, a large quantity of water was added with the lime and the whole warmed for a short time and then evaporated down, extraction took place far more readily. In Experiment 7 the water content was reduced to 15 per cent. and in Experiment 8 to 33 per cent. It is rather remarkable to find that the second mixture gave up its caffeine much more readily than the first, since it might be expected that, owing to the great solubility of caffeine in hot water, the mixture with the higher water content would retain the caffeine more tenaciously. With 33 per cent. of moisture the water remains absorbed in the fluff, but if the moisture content is increased much beyond this point the water separates and carries down brown colouring matter into the toluene solution. In the two experiments just mentioned excess of water was added to allow thorough mixing and permeation of the fluff by the lime in solution. In Experiment 21 the calculated quantity of water to produce 33 per cent. moisture was added and the mass extracted without evaporation. Although nearly the same total yield of caffeine was obtained as in Experiment 8 it will be noticed that the first extraction gave a much lower yield indicating that an appreciable time is necessary under these conditions to make the caffeine available for extraction.

In the subsequent experiments mixtures of fluff and juice were used, and it was found that more than six parts of juice could not be mixed with one part of fluff without making the evaporated mixture too sticky to be readily extracted. In all cases evaporation was continued until the moisture content was 33 per cent., and comparative experiments were made using various quantities of lime and magnesia. Experiments 11, 12 and 9 show that a very large excess of lime is not necessary, while 14 shows that the lime may be partially replaced by magnesia without appreciably affecting the extraction.

A second series of experiments was carried out with toluene as solvent but using sodium carbonate instead of lime or magnesia. Experiments 22 to 27 show clearly the effect of reducing the moisture content of the charge. In these the fluff was mixed with anhydrous sodium carbonate, the water added and the whole mixed in a mortar and warmed on a water bath until the correct moisture content was attained. It will be seen that the yield of caffeine diminished with the moisture content of the charge until on complete drying only 12-16 per cent. was extracted. In Experiment 25 less water was added than in Experiment 24, other conditions being the same, and a large reduction in yield resulted.

In the subsequent experiments much less sodium carbonate was added in the form of a concentrated solution and equally good results were obtained. A comparison of Experiments 28, 29 and 30 shows that, under these conditions, there is not a great difference between the yields from mixtures with 25 and 30 per cent. moisture content, and that it is not necessary to add excess of water and evaporate it off.

In Experiment 31 only 5 per cent. of sodium carbonate was used without detriment to the yield, and in Experiment 32 good results were obtained from a mixture of fluff and juice. In this case the juice was concentrated before being added so that it was equivalent to the 300 cc. used in previous experiments.

With regard to the use of other solvents it will be seen from Experiment 10 that petrol is not at all satisfactory. Commercial alcohol (about 86 per cent.) in the presence of excess of lime extracts a large proportion of the caffeine, but not nearly as rapidly as toluene does. In addition, a large quantity of brown colouring matter soluble in water is also extracted, and this complicates the subsequent isolation of caffeine. In Experiment 19 in which the charge was dried in the hope of reducing the amount of foreign matter, the total extract was 4·03 grams or nearly four times the weight of the caffeine in the extract.

The quantity of green colouring matter extracted is rather uncertain and no definite conclusions can be drawn as to the effect of the different solvents or of alkalis on the amount extracted. The maximum amount obtained is about 0·8 of the total caffeine in the fluff and this is of importance in connection with the subsequent separation of the two materials. When sodium carbonate is used with toluene as solvent the quantity extracted is fairly constant and is usually between 0·3 and 0·4 of the total weight of caffeine present.

It is worthy of note that this green matter is extracted very readily so that the colour of the solution may be used as a guide to the efficiency of the washing of the fluff with the fresh solvent. On the small scale the solution became colourless after about five syphonings, but on the larger scale considerably more were required, indicating the formation of pockets and insufficient draining.

To summarise, caffeine can be readily extracted from tea fluff or mixtures of tea juice and fluff by means of toluene or hydrocarbon.[1] Between 80 and 90 per cent. of the caffeine can be obtained in two hours.

In order to obtain this result it is necessary to add a considerable quantity of lime or magnesia and to boil the fluff with water if no juice is used. The mixture must then be dried until the moisture content reaches about 33 per cent. Alternatively the fluff may be mixed with a solution containing about 5-8 per cent. of sodium carbonate on the weight of the fluff and sufficient water to make the moisture content of the charge about 33 per cent. Under these conditions over 90 per cent. of the caffeine can be extracted in three hours with toluene and the decomposition is less than when lime is used.

IX. LARGER SCALE EXTRACTION EXPERIMENTS.

Extractions on a larger scale were next made. In one series tea fluff was mixed with lime or magnesia and with juice or plain water in the proportion of three parts of liquid to one part of fluff. The larger proportion of 6 to 1 adopted in the small scale experiments was not used owing to the difficulty of obtaining sufficient juice, and to the fact that the evaporation of such a large quantity of water would be an expensive operation in big scale work. The mixture was heated in a steam jacketted pan until water would no longer drain from the solid, and the whole was then dried in the open air or transferred to an iron tray heated by exhaust steam and raked until the requisite moisture content was reached. Analysis showed that this operation resulted in a loss of between 4 and 5 per cent. of the total caffeine, a figure much larger than was expected. In the other series tea fluff was simply mixed with a sodium carbonate solution containing enough water to bring the moisture content to the required figure without evaporation. The charge weighing about 250 lbs. was put into a cylindrical cast iron extractor of 12 cu. feet capacity and extracted with the solvent. The operation of the extractor was similar to that of a Soxhlet apparatus, but the solution was run to the boiling vessel through a pipe and the rate of flow controlled by means of a cock. By this means the extraction could be performed by continuous percolation or intermittently. The latter method was found to be more satisfactory, as in the former the distribution of solvent was not uniform and pockets of unextracted material remained. The reflux con-

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[1] This process is covered by Ind. Pat. 5095, 1919.

denser used at first had a surface of only 10 square feet and was rather small for the plant, as thirty minutes were required to fill the extraction vessel. Consequently twelve fillings and emptyings occupied six hours, whereas the small scale experiments required only three hours for the extraction of nearly all the caffeine. In the larger extractor the same quantity of solvent extracted far less caffeine, possibly owing to the greater pressure and the resulting compactness of the material.

In Experiments 8, 9 and 10 a larger condenser with a surface of 70 square feet was used, and, with the aid of this, the time required for filling the extractor was reduced to 15 minutes, and the whole extraction completed in 9 to 10 hours.

At the end of an extraction, steam was blown through the fluff to remove the solvent and the solvent and condensed water separated in a separator which formed part of the apparatus. The solvent was distilled from the extract until the volume was reduced to about 10 gallons and this residue was forced into a small separate steam jacketed still; 1 gallon of water was added and the mixture boiled. After standing for a short time the aqueous layer containing a large proportion of the caffeine was run off. The green colouring matter remaining in the still was boiled three or four times with successive quantities of 0·5 gallon of water to wash out the caffeine thoroughly, and finally the remaining toluene was distilled from the green colouring matter and wax. If attempts were made to hasten the extraction with water and to reduce the number of washings by distilling off the major portion of the toluene before adding water, an emulsion formed which could only be broken with great difficulty.

Table X shows the results obtained in these experiments.

Speaking generally, the results obtained correspond with those which were anticipated from the small scale experiments, the chief difference in the two sets being, as already mentioned, the longer time taken by the larger scale experiments.

The main conclusions which may be drawn from the results are as follows :—

1. Hydrocarbon is a less satisfactory solvent than toluene, doubtless owing to the lower temperature of extraction and consequent decreased solubility. Experiments 5 and 6 which were carried out under identical conditions, except for the solvent, show this clearly. In Experiment 5 an extraction of 27 hours duration, during which the extraction vessel was filled with solvent 28 times, the caffeine extracted was 66·0 per cent., while in Experiment 6 the corresponding figures were 18 hours, 15 fillings and 76·2 per cent. yield.

TABLE X.

Results of large scale extraction experiments.

No. of experiment	Weight of fluff lbs.	Weight of juice lbs.	Lime as CaO lbs.	Magnesia as MgO. lbs.	Weight of added water lbs.	Percentage of moisture in charge	Time of extraction in hours	Solvent	Percentage of total caffeine in charge					
									As crystals	In Mother liquors	In colouring matter	Un extracted	Total	Decomposed or lost
1	90	176	16	...	100	32	17	Hydrocarbon.	47·6	13·6	3·5	17·5	82·2	17·8
2	100	86	9	8	210	27	18	,,	50·5	11·7	0·7	12·5	75·4	24·6
3	100	86	...	16	210	29	18	,,	54·7	5·4	1·8	18·0	80·9	19·1
4	175	...	8	8	525	29	15	,,	51·6	20·5	1·6	12·0	85·7	14·3
5	175	...	8	8	525	25	27	,,	64·3	1·0	0·7	10·6	76·6	23·4
6	175	...	8	8	525	25	18	Toluene	72·2	3·5	0·5	7·0	83·2	16·8
				Na_2CO_3										
7	175	...	...	13	41	25	28	,,	81·6	5·6	0·5	8·5	96·2	3·8
8	175	...	...	13[1]	47	26	12	,,	72·9		1·2	8·6	82·7	17·3
9	175	...	...	13	41	25	10	,,	87·9		1·4	5·4	94·7	5·3
10	175	...	...	13	70	33	9	,,	88·1		1·4	7·5	97·0	3·0

[1] Mainly sesquicarbonate

2. When lime, or mixtures of lime and magnesia or even magnesia alone, are used there is an appreciable loss of caffeine by decomposition. In Experiments 1 to 6 this was approximately 1 per cent. per hour in addition to the 4 to 5 per cent. lost during the preparation of the charge. The loss in Experiment 2 is abnormal and may possibly be due to the fact that the charge was allowed to stand a fortnight after analysis during repairs to the extractor.

3. When sodium carbonate is used, the loss of caffeine is greatly reduced and the figures shown in Experiments 7, 9 and 10 are probably mechanical losses. The results of Experiment 8 are not very clear, but in this case a crude soda consisting mainly of sesquicarbonate was employed and the results were not satisfactory. Another advantage of the use of sodium carbonate is that the addition and subsequent evaporation of a large excess of water, which appears to be necessary in the case of lime, can be avoided.

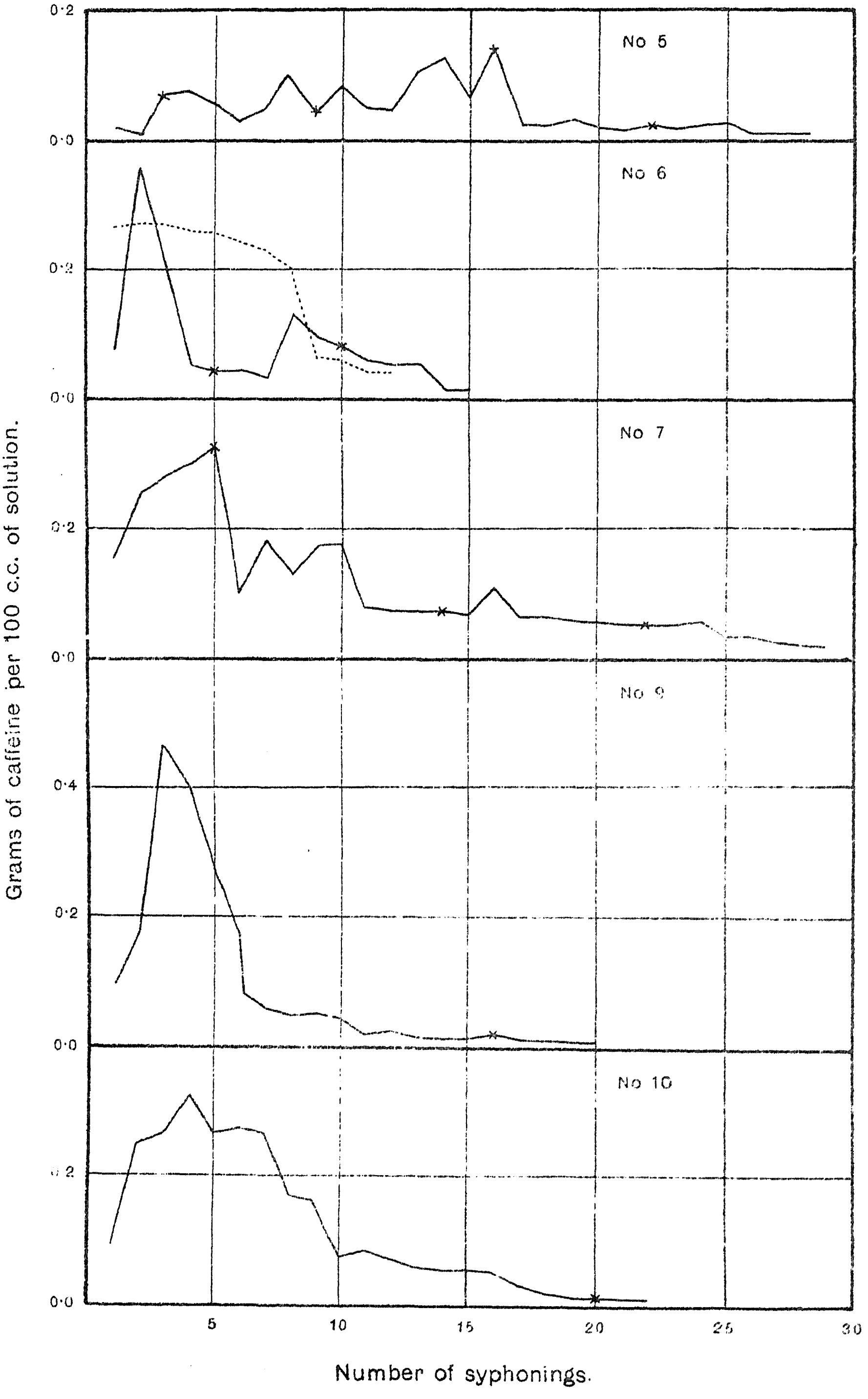
4. Experiments 8, 9 and 10 in which the larger condenser was used show that the time of extraction can be greatly reduced by increasing the supply of solvent. There is every reason to believe that by still further increasing the supply and by fitting the extractors with an efficient stirring apparatus the time could be reduced to that required in the small scale experiments, viz. 3-4 hours.

During some of the large scale experiments, which were carried out intermittently, samples were taken of the solution each time it was run out of the extraction vessel and the caffeine content determined. It was not possible to obtain a fair sample of the whole of each extract and so a sample was taken by withdrawing some of the extract during its passage from the extraction vessel to the vessel in which it was boiled when half the liquid had run down. The solvent was distilled from 100 cc. of this sample and the caffeine estimated in the usual way.

The curves in Fig.II show the results obtained for five extractions, In these the number of grams of caffeine in the 100 cc. sample is plotted against the number of fillings of the extractor. In the first three extractions several days were required for completion of the experiment and the extractor was allowed to cool overnight. The points at which this was done are marked by crosses. It will be noticed that on starting or resuming an extraction an appreciable time elapses before the maximum concentration of caffeine is reached, as the charge takes some time to become warm. Curve 2 shows very clearly the effect of uneven packing of the charge. Although most of the caffeine appeared to be extracted at the end of the first day, on standing overnight the solvent was able to diffuse throughout the mass, resulting in an increased yield the next day.

Figure II

Rate of extraction of caffeine by hydrocarbon and toluene.



The dotted curve in Experiment 6 gives the results obtained on extracting 80 grams of the big charge in a Soxhlet and taking a 10 cc. sample at each syphoning. The results are calculated so as to show approximately the weight of caffeine which would have been obtained if the weight of the charge and solvent had been the same as in the large scale experiment and if 100 cc. samples had been taken. It will be seen that the types of curve are very different and that in the small scale experiment the original solvent is washed out very completely after eight syphonings instead of the six indicated on p. 197.

X. PURIFICATION OF THE EXTRACTED CAFFEINE.

The first three of the aqueous solutions of caffeine obtained from the concentrated toluene extract as described on p. 202 usually deposited crystals of caffeine on cooling. These were contaminated by part of the green colouring matter which could not easily be separated from the solution owing to its waxy nature. If, however, the hot solution was treated with a very small quantity of basic lead acetate solution, a precipitate was formed which carried down the colouring matter and the solution could be readily filtered. The crystals of caffeine which separated on cooling were greenish in colour. They were recrystallised four times from four times their weight of hot water and finally decolorised with 2·5 per cent. of their weight of decolorising charcoal. The crystals thus obtained were quite white, contained about 6 per cent. of water and conformed to the British Pharmacopœia tests for purity.

XI. EXTRACTION OF CAFFEINE WITH SUPERHEATED STEAM.

As caffeine is said to sublime readily at about 180°, and may frequently be seen in the vicinity of tea driers, in which the tea is subjected to a temperature much below this, it seemed not unreasonable to hope that it might be possible to remove the caffeine from tea fluff by merely heating, or, at least, by heating in a current of superheated steam or indifferent gas. The two Japanese patents mentioned on p. 180 appeared to indicate that one of these methods might be commercially practicable, and consequently a few experiments were carried out to ascertain the nature of the results.

Direct heating of tea fluff on a watch glass to temperatures well above its decomposition point produced a sublimate containing merely a trace of caffeine and experiments on these lines were not continued.

100 grams of fluff or in the third experiment a mixture of 75 grams of fluff and 75 grams of magnesia was placed in a distilling flask, immersed in an oil bath, and superheated steam passed through the fluff. 800 cc. of distillate was collected in portions of 50 cc. and each portion evaporated slowly on a water bath and the residue weighed Table XI shows the results obtained.

TABLE XI.

Results of treating tea fluff with superheated steam.

No. of Experiment	Temperature of steam	Weight of soluble residue in grams	Percentage yield
1	155°	0·160	5·3
2	180–190°	0·165	5·5
3	180–190°	0·320	14·2

In the third experiment in which magnesia was used, the weight of the total distillate was 1·28 grams, but most of this was insoluble in water.

As far more satisfactory results were obtained by the extraction process, these experiments were not continued.

In conclusion, we wish to thank Miss M. Bain and Miss J. M. Kelsall for much assistance during the early part of the work, and the managers of tea estates who kindly supplied samples for analysis.

XII. SUMMARY.

1. The distribution of caffeine in the tea plant is described and a number of analyses of the caffeine in samples of tea fluff from different localities are given.

2. The usual methods of preparing caffeine are outlined.

3. A description is given of experiments on extraction from tea fluff by means of hot water. These show that the method is inefficient, that it is impossible to obtain concentrated solutions of caffeine directly, that large quantities of lead acetate are required, that at least 200 lbs. of water have to be evaporated for every 1 lb. of caffeine and that the losses are considerable.

4. It is shown that it is possible to obtain caffeine from tea juice by the lead acetate process, but it is difficult to obtain good yields and it is doubtful whether this method would be of any commercial value.

5. The solubilities of caffeine in a number of solvents at different temperatures are given and it is concluded that benzene and toluene, especially the latter, are suitable solvents for carrying out extractions on a commercial scale.

6. When tea fluff is treated with a solvent it is found that not all the caffeine is dissolved, but a state of equilibrium is set up owing to the adsorption of the caffeine by the fluff. Average tea fluff is in equilibrium with an aqueous solution containing about 1·3 per cent. of caffeine, that is to say, a solution of this concentration will not dissolve any caffeine from tea fluff. If tea fluff is treated with lime and five times its weight of water only about 80 per cent. of the caffeine goes into solution. If eight parts by weight of toluene at the boiling point of water are used as solvent, only 8 per cent. of the caffeine dissolves if the fluff is previously dried, but in presence of an alkali and a suitable quantity of water, the proportion dissolved may be raised to over 70 per cent.

7. Caffeine is very appreciably decomposed on prolonged heating with lime at temperatures between 90 and 100° C. in presence of water or toluene and water. If the lime is replaced by magnesia the amount of decomposition is lessened, while if sodium carbonate is used the decomposition is very slight.

8. Caffeine is not readily extracted from dry tea fluff by means of volatile solvents. Good yields can be obtained by adding an alkali, preferably sodium carbonate, and water. If this is done it is possible on a small scale to extract 95 per cent. of the caffeine in three hours using toluene as solvent.

9. The best conditions for the extraction of caffeine on a larger scale are similar to those found in small scale experiments but a longer time is required for the process.

10. A suitable method for obtaining pure caffeine from the crude extracts is described.

11. The direct recovery of caffeine from tea fluff by distillation with superheated steam does not appear to be a practicable process.

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