TABLE III.—ANALYSES OF MAPLE SYRUP FOUND ON THE MARKET.

Serial number.		Total solids. Per cent.	Sucrose by Clerget's formula. Per cent.	Hortvet number.[1]	Lead number.	Total ash. Per cent.
15988	Pure	66.98	62.4	1.00	2.03	0.75
15989	Pure	67.29	61.6	0.69	1.61	0.60
16037	Pure	66.40	59.5	1.24	1.89	0.54
15929	Adulterated[2].	66.40	65.4	0.15	0.66	0.14
15932	Adulterated	66.90	65.4	0.15	0.48	0.16
15945	Adulterated	65.81	.....	0.22	0.87	0.23
15948	Adulterated	67.61	67.8	0.07	0.52	0.04
15961	Adulterated	63.18	.....	0.07	0.10	0.02
15967	Adulterated	68.62	67.6	0.07	0.02	0.04
15970	Adulterated	66.58	65.2	0.11	0.19	0.19
15971	Adulterated	69.49	68.4	0.11	0.43	0.07
15982	Adulterated	64.53	61.9	0.15	0.17	0.17
16005	Adulterated	65.57	.....	0.15	0.12	0.04
16006	Adulterated	66.13	65.2	0.11	0.66	0.08
16035	Adulterated	65.33	60.0	0.12	0.92	0.14

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ON THE DETERMINATION OF CARBON DISULPHIDE AND TOTAL SULPHUR IN COMMERCIAL BENZENE.

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CRUDE, unwashed benzene, or the so-called "benzol light oil," contains as certainly identified sulphur compounds, hydrogen sulphide, carbon disulphide, thiophene and its homologues. There are doubtless others among the unsaturated compounds which become eliminated in the first stage of benzene purification, the washing with concentrated sulphuric acid. There is left after this treatment in the lower-boiling fractions derived from the washed benzene, as a main impurity carrying sulphur, carbon disulphide. Thiophene, as well-known, represents the chief of other sulphur bodies present.

I. THE DETERMINATION OF CARBON DISULPHIDE.

The principle underlying the method seemingly most widely practiced is that of the transformation of carbon disulphide by means of alcoholic potash into potassium xanthate, utilizing this

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[1] Cubic centimeters of lead precipitate from 5 grams of the material.

[2] The adulterated samples were mixtures of maple syrup and refined cane-sugar. Some were labeled as compounds and therefore were not legally adulterated.

substance as a medium of separation for the sulphide. For the determination of the sulphide the xanthate has variously been weighed as such, converted into cuprous xanthate, and again titrated with cupric sulphate solution. Nickels[1] seems first to have applied the xanthate reaction to a separation of carbon disulphide from benzene. The volumetric method referred to originated with Macagno[2] with a view, however, of applying the process to the assaying of carbon disulphide preparations.

The method of Nickels[3] to determine the sulphur finally by weighing the potassium xanthate or cuprous xanthate derived from it *as such* is attended by several inaccuracies. When operating with the potassium salt it must be separated by filtration and washed with ether. The mother-liquors are merely drawn or drained off and leave a precipitate contaminated by adhering alkali not removed by the ether. It is constantly undergoing decomposition on exposure to air. The cuprous salt is more stable but cannot be brought to constant weight without decomposition even by moderate warming after water-washing. By ether treatment of the precipitate freed from the mother-liquors, a more successful drying might result. In view of the somewhat unstable character of the compound, however, the determination as copper oxide, after ignition of the precipitate, promised more satisfactory results. Much uncertainty exists apparently as to the exact composition of the so-called cuprous xanthate. If constituted as represented by the formula $(CS.OC_2H_5S)_2Cu_2$, the ratio of copper oxide produced to carbon disulphide entering into the formation of the xanthate should be 1.0:0.9563. In establishing the basis of his volumetric method, Macagno made some determinations of the ratio and found 1.0:1.931 not much varying from *twice* the theoretical. Others have obtained similar results indicating approximately the relationship $2CS_2 : CuO$. As evidently cuprous xanthate is not the compound under consideration, judging from the ratios thus discovered, and recalling the instability of the body resulting from the action of cupric sulphate on potassium xanthate, a reopening of the question as to the ratio of the copper compound obtained on ignition of the xanthate produced by a known weight of carbon dioxide seemed

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[1] Chem. News, 43, 148.

[2] Ibid. 43, 138.

[3] Attributed to him by Allen: Comm. Organ. Anal.

justified. An investigation appeared the more desirable because of a strong probability of a variation in composition with changing conditions of formation. Experiments were, therefore, made, having in mind a process for the separation and determination of carbon disulphide contained in benzene by means of the xanthates, the method being adapted to convenient manipulation and conditions easily realized and thus maintained constant. The ratio of copper oxide, yielded by the yellow xanthate upon ignition, to the carbon disulphide from which it was derived under the given circumstances was made the subject of the experiments, an account of which follows:

1. Determination of the Ratio of the Copper Ignition-Residue to Carbon Disulphide.

That the ratio might be an expression of the many experimental factors in a determination of carbon disulphide in benzene, known weights of a perfectly pure sulphide were dissolved in a specially prepared benzene, the sulphide transformed into potassium xanthate, which was separated and determined, as to be described.

The Separation of the Carbon Disulphide as Xanthate.—As intimated above, the matter-of-course precaution was taken to apply a preparation of carbon disulphide of high purity, and the usual manipulations in the weighing and transfer of so volatile a substance without loss were employed. The weighed portions of the sulphide were added to about 75 cc. of pure benzene contained in a glass-stoppered flask of 250 cc. capacity. Besides the benzene the flask already contained for each 0.1 gram of carbon disulphide about 1 cc. of a saturated alcoholic solution of potassium hydroxide. The sulphide was then liberated from the weighing vessel and the mixture agitated fifteen to twenty minutes. The potassium xanthate formed was dissolved by addition of water, and the aqueous xanthate solution and benzene transferred to a separating funnel. The solution was drawn off and the benzene well washed. The extraction was repeated with about three-quarters of the original amount of potassium hydroxide solution and a third time should a separation of xanthate crystals occur in a second extraction. The extracts and washings were diluted to 500 cc. and aliquot parts applied for precipitation.

The Precipitation as Cuprous Xanthate and Determination as

Copper Oxide.—The alkaline xanthate solution was acidified with acetic acid, used well diluted and in very slight excess. Immediately the cold solution was treated with copper sulphate solution (1 : 5) in distinct but not great excess. During standing for one to one and one-half hours after the precipitation, the precipitate was repeatedly stirred. It has most agreeable qualities for quantitative manipulations. Filtration and water-washing are expeditious and perfect. The filtrate passed the filter clear as did the washings, as just implied, but upon standing for some hours, for instance over night, slight further precipitation invariably took place. In the experiments under discussion, this precipitate was collected and added to the main portion. In the usual technical analysis the amount of xanthate here concerned is so small as to become negligible. This second precipitation is presumably caused by dissolving of the compound in the washings in which it is more soluble than in the liquors in which it forms.

At once after the washing the precipitate was removed to a porcelain crucible, dried and ignited. A constant weight was easily obtained. The product of the ignition, in the main copper oxide, may also contain, where large precipitates are involved, some cuprous sulphide, a consideration which evidently in nowise disturbs the ratio sought.

2. *The Data Obtained.*

In the table below are found the results of a number of determinations of the CS_2-CuO ratio. No pretense is here made to an exhaustive investigation of the subject. Those points only which plainly require consideration for the purpose of establishing a method of sufficient accuracy for technical application were given attention. The variation in the ratios developing under circumstances defined in the table indicate need of still more detailed limitation of conditions. The relation of the xanthate to the quantity of alcoholic potash by which it is formed, the acidity and dilution of the solution upon precipitation of the copper salt and the excess of copper sulphate are all factors which, when exactly determined and considered, would eliminate in all probability, variations in the ratios appearing under identity of those conditions thus far investigated.

THE RATIO OF COPPER OXIDE TO CARBON DISULPHIDE UNDER VARYING CONDITIONS OF EXPERIMENT.

No.	CS_2.	Excess $CuSO_4$.	Age of xanthate solution.	Time for precipitation.	CuO.	CuO : CS_2. CuO = 1.0.
3	0.06038	Slight	Fresh	0 hrs.	0.0349	1.730
4	0.06038	Moder.	"	16 "	0.0379	1.593
7	0.06038	"	2-3 das.	1½ "	0.0354	1.706
1	0.08534	Large	Fresh	¾ "	0.0488	1.749
2	0.08534	Moder.	"	¾ "	0.0474	1.800
5	0.08534	Slight	3 das.	1 "	0.0494	1.728
8	0.13710	Moder.	Fresh	¼ Stir.	0.0747	1.825
9	0.13710		2 das.	20 hrs.	0.0805	1.703
10	0.13710	Moder.	3 "	1½ "	0.0770	1.780

In comparison with the results of former work, a much *lower ratio* is seen to exist under the circumstances detailed. The average is 90 per cent. of the Macagno ratio.

Among the factors taken into account in the present series of experiments, those of the size of the precipitate (quantity of carbon disulphide present) and time of standing before filtration appear as of most significance. The results from the use of 0.06 gram of carbon disulphide are about 5 per cent. lower than when 0.14 gram was applied. The influence of time on the precipitation is shown by 3 and 4, and again by 9 and 10; the former instances, for the longer period, show an 8 per cent. lower ratio; the latter, one by 4 per cent. lower. As representing the results to be obtained by the method described, No. 7 for 0.06 CS_2, Nos. 2 and 5 for 0.085 CS_2 and No. 10 for 0.14 CS_2 have been selected as working factors and the average as a general working factor. An extreme difference of about 4.0 per cent. exists. With a benzene containing 2 per cent. carbon disulphide, a variation of less than 0.10 per cent. would be involved by the use of the lowest and the highest factor. The average of 1.750 was adopted for general practice.

WORKING FACTOR IN RELATION TO CARBON DISULPHIDE CONCERNED IN ITS PRODUCTION AND THE AVERAGE FACTOR.

CS_2.	Working factor.	Average factor.
0.06038	1.706	1.676
0.08534	1.764	1.759
0.13710	1.780	1.773
Average,	1.750	1.736

Below are tabulated several results of carbon disulphide determinations in benzene samples, 90 and 100 per cent., by the method derived from the data secured in the above experiment.

RESULTS OF ANALYSES BY THE METHOD DESCRIBED.

Sample No.	Determination. I.	Determination. II.	Difference.
1	0.809	0.765	0.044
2	0.475	0.477	0.002
3	0.442	0.414	0.028
4	0.743	0.764	0.003

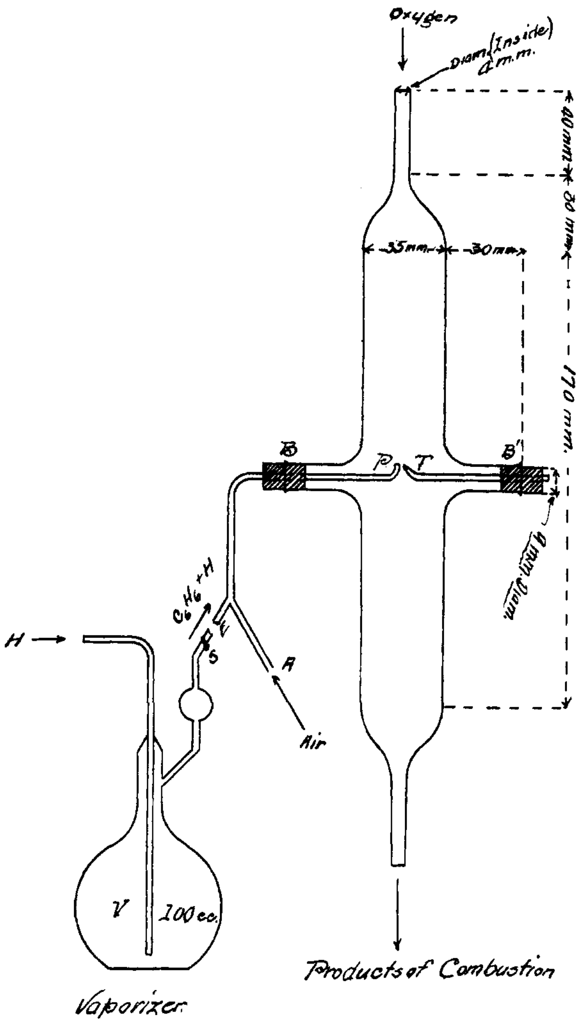
II. DETERMINATION OF TOTAL SULPHUR IN BENZENES.

The determination of total sulphur in benzene by the usual method of Carius for organic compounds is wholly impracticable. Acting in part on suggestions extant, as a result of the work of the older and more recent investigations in this field, it was sought to accomplish the purpose by vaporizing the hydrocarbon and combustion of the gas-mixture in an atmosphere of oxygen. The products of the combustion were passed into a suitable absorption medium and determined by familiar methods. The experimentation here involved related especially to a *form of apparatus* well adapted to the combustion and resulted in the vertical combustion-tube described in the immediate context. It was further made to embrace several features concerning the absorption and determination.

1. The Apparatus.

The hydrocarbon is contained in a small flask of about 100 cc. capacity of the form shown in the sketch accompanying at *V*. It is connected at *H* with a supply of sulphur-free hydrogen. The outlet beyond the stopcock *S* is connected with the Y-tube attached to the arm *B* of the combustion-tube. The bulb on the exit-tube serves to prevent the spurting of condensate into the burner, which becomes possible when heat is required to assist the vaporizing.

The combustion-tube is shown in the essential features in the sketch. The Y-tube *E A* carries the burner, as seen, at *P*. The latter is a platinum piece slipped gas-tight over the glass tube. The burner-tube is joined by a short piece of rubber tubing to the arm *B*. At *T* is the tip for the pilot-flame. It is likewise of platinum, and is fused into a glass carrying-tube in the position indicated. In each arm, but not shown in the drawing, is a coil of platinum foil. It extends from the stopper nearly to the center of the combustion-tube. The arm-space is filled as completely as possible, only room required for the free passage of the burners being left. The upper end of the combustion-tube is connected



with the oxygen supply. The gas is passed for purification through a calcium chloride tower filled with pieces of caustic soda. Beside this jar stands a second charged in the same manner and serves for the purification of the air forced in at *A*. The connections on the jars are such that at the end of the combustion air may be turned into the apparatus from above, through the oxygen jar, for the purpose of aspiration, without disconnecting at any point.

The hydrogen for the pilot-flame is purified by passage through a small wash-bottle containing a solution of caustic soda. The arrangement is further required in aiding the regulation of the flow of gas. To observe the rate of the oxygen supply and deliver it comparatively dry to the purifying apparatus, thus prolonging the serviceability of the latter, the gas passes from the holder first through glycerol.

The combustion-tube is wrapped in asbestos cloth for protection against drafts, a small opening only being left opposite the flames to permit of their observation. In the coolest part of the tube, the arm, a dangerous accumulation of water may take place. Warming becomes therefore necessary and is efficiently and automatically accomplished by the rolls of platinum foil already referred to. In this form the gas combustion-tube has proven itself well adapted to its purpose; the cracking of the tube in service is rare and then usually the result of inadvertence.

2. *The Combustion.*

The sample of benzene, about 5 grams, having been weighed in the vaporizer and all connections established, the apparatus is first filled with oxygen. The pilot-flame tube is withdrawn, a small flame started and the burner returned to its position in the combustion-tube. When first inserted, the flame must be larger than it is expected to maintain it, otherwise by the pressure existing in the tube, it will be so reduced in size as to be extinguished by the draft in the apparatus. The flame is adjusted to the smallest possible size consistent with keeping it alive. Care is taken to so place it that it is close to the edge of the burner-tip and will thus ignite the vapors instantly upon their arrival. With the arm *A* of the burner-tube and the stop-cock *S* closed, the hydrogen is turned into the vaporizer and thence cautiously admitted to the burner. Due to the downward movement of the oxygen, the vapors ignite even before reaching the tip of the burner, if the rate of admission is a little too slow. The flame appears at the tip brilliantly luminous. Increasing its size somewhat, air is admitted and the combustion continued with a half-luminous flame about 1 inch in length. Since some variation in the pressure of the gas entering the burner is scarcely to be avoided, the operation requires some oversight. The complete disappearance of benzene from the gases supplied to the burner may be sharply detected by the appearance of the flame. A perfectly non-luminous flame denotes with certainty the end of the combustion. The stop-cock *S* is then closed, the pilot-flame extinguished, the oxygen turned off, and the passage of air through *A* continued for a few minutes. *A* is then closed and the air turned into the upper end of the combustion-tube by the simple setting of the stop-cocks on the air and the oxygen drying jars.

The combustion of 5 grams of benzene may be accomplished in about three hours. This applies to 90 and 100 per cent. benzene; light oil, with its less volatile constituents, requires a longer period. Warming the vaporizer hastens the operation and is necessary to completion of the process within a reasonable time.

3. The Absorption.

The gases and vapors leaving the combustion-tube contain the sulphur of the sample mainly as sulphur dioxide, but doubtless contain some sulphur trioxide as well. Mabery[1] states that in the form of apparatus devised by him for a somewhat similar purpose, the sulphur is contained wholly as sulphur trioxide notwithstanding the combustion was carried out in air, with the latter, however, in enormous excess. Special tests upon the gases from the above combustion apparatus detected sulphur dioxide unmistakably in large quantity. Several of the familiar absorbing media for the sulphur oxides were experimented upon and brominated sodium carbonate adopted for gravimetric determinations. The much more expeditious volumetric method of Mabery,[2] who used fractional normal alkali for absorption, was made the subject of some experiments.

In all cases glass-stoppered wash-bottles of about 250 cc. capacity were employed as receptacles for the absorber. Two were found adequate to the ordinary purpose.

The *sodium carbonate* and *bromine mixture* for absorption contained 25 grams of the purified crystallized salt dissolved in 110 cc. of water. The solution was distributed in equal volume between the two bottles. To the first was added more than an excess of bromine in saturated aqueous solution to oxidize the whole of the sulphur to be absorbed, assuming it present entirely in the form of sulphur dioxide. Ten cc. of the bromine solution

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[1] Am. Ch. J. 18, 211.

[2] Pr. Am. Acad., Vol. 30.

are abundant for percentages up to 1.0. In each succeeding bottle of the absorber one-half the above quantity suffices.

With the carbonate-bromine absorber, as with all others tried, the formation of white fumes in the atmosphere of the absorbing bottles is a matter well-known to those who have dealt with the problem of the oxidation and absorption of the sulphur oxides, but perhaps still calling for some comment in this connection.

In all cases the fuming was most marked at the beginning of the combustion, at a time therefore when the vapors were most highly charged with sulphur in the form of carbon disulphide. Further, the higher the percentage of sulphur, the more voluminous the fume-formation, confirming the conclusion from the first observation that the fumes are carriers of sulphur. The subject is mentioned thus in some detail as emphasizing the necessity of a complete suppression of the fumes within the absorber if the utmost accuracy is to be attained. The accomplishment of this refinement, with conditions as set forth, has as yet not been fully realized in any simple manner. The limited and intermittent work which it has thus far been possible to devote to this phase of the determination has shown that, with an absorber made up of as many as four wash-bottles and with benzene samples of about 0.50 per cent. carbon disulphide, in the third and fourth bottles as a rule, the quantity of sulphur absorbed is practically the same, and an amount corresponding to somewhat less than 1 mg. of barium sulphate. Although numerous other devices (than increasing the number of absorbing bottles) for the promotion of extent and time of contact by the combustion gases with the absorber have been applied in conjunction with most of the practically available absorbing reagents, little or no better results than just indicated have been obtained. For technical purposes, however, this efficiency fully satisfies all requirements. The loss of sulphur sustained, by the use of two absorbing bottles as practiced, is not greatly beyond the limit of experimental error.

The use of N/50 *sodium hydroxide* gave, in the analysis of the 90 and 100 per cent. benzenes first experimented with very satisfactory results. Later efforts to apply the method to crude benzenes were unsuccessful. Time has not yet been available to determine the point of difficulty. The absorbing apparatus was composed in this instance likewise of two bottles each charged with alkali in excess to the extent of 15 to 20 per cent. of the possible maximum requirement. Usually, about 0.5 cc. of the N/50 sodium hydroxide in the second bottle was used, and represents 0.003 per cent., with a total percentage, as above, of about 0.40.

4. Determination of the Sulphur.

The *gravimetric* determinations were made with the usual precautions current for accurate work.

For the *volumetric* method, as already stated, N/50 sodium hydroxide was contained in the absorbing apparatus. To determine the excess of alkali N/10 sulphuric acid was found most practicable. Since the sulphur is present partly as sulphite, before titration the solution was treated with a few cubic centimeters of neutralized hydrogen peroxide; 5 to 6 cc. of a 2 per cent. solution sufficed for the main portion. The contents of the second bottle were treated with half the amount. The titrations were made in the absorption bottles, and with methyl orange as indicator.

However determined, attention need scarcely be called to the necessity of recovering the sulphuric acid remaining after the combustion upon the walls of the tube. When special accuracy is an object, the residues left in the vaporizer, especially by crude benzene, become a consideration.

5. Comparison of the Results Obtained.

The results in the table following were from combustion of the same sample of benzene and, as noted, by both methods of determination.

GRAVIMETRIC AND VOLUMETRIC DETERMINATIONS COMPARED.

	Method.			
No.	Grav.	:	Vol.	No.
2	0.379		0.376	8
3	0.350		0.345	9
4	0.378		0.379	10
5	0.370		......	...
6	0.370		......	...
Average,	0.370		0.367	

Very satisfactory determinations have also been made with benzene containing as much as 5 per cent. carbon disulphide, the results being concordant within 0.10 per cent.

Insuring perfect and convenient combustion, the apparatus could be extended in its application to the determination of total sulphur in gases and vapors of whatever description. Fuel and illuminating gases are here in mind. It could further doubtless be made to lend itself in many instances advantageously to sulphur determinations in the ultimate analysis of organic compounds.

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THE SYSTEM LIME, GYPSUM, WATER, AT 25°.[1]

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THE three-component system—lime, sulphuric acid, water—has been studied in this laboratory by Cameron and Breazeale.[2] In this work the composition of solutions containing an excess of the acid has been investigated over a wide range of concentration. In all solutions up to 300 grams of SO_3 per liter the stable solid phase is gypsum. We have investigated the composition of solutions in which the lime has been in excess of the acid.

Two series of solutions have been prepared, one, various lime solutions to which solid gypsum has been added, and the other, various gypsum solutions to which lime has been added. These bottles were put in the thermostat at 25° and were rotated constantly for a period of two weeks. At the end of this time known volumes were analyzed for lime and for sulphuric acid. These results are given in the following table:

TABLE I.

SO_3 per liter. Grams.	CaO per liter. Grams.	Solid phase.
0.0	1.166	$Ca(OH)_2$
0.230	1.302	"
0.392	1.424	"
0.562	1.608	"
0.714	1.742	"
0.934	1.876	$Ca(OH)_2$, $CaSO_4.2H_2O$
0.961	1.612	$CaSO_4.2H_2O$
1.013	1.320	"
1.090	1.112	"
1.128	0.966	"
1.194	0.898	"
1.251	0.875	"

[1] Published by permission of the Secretary of Agriculture.

[2] J. Physic. Chem. 7, 571 (1903).