quires.   Probable causes of this abnormal lowering have been considered.

6. The practical application of the use of ammonium thiocyanate in the absorption of ammonia has been considered.

NEW HAVEN, CONN., and TROY, N. Y.

THE COPPER FLAME TEST FOR HALOGENS IN AIR.[1]

BY ARTHUR B. LAMB, P. W. CARLETON, W. S. HUGHES AND L. W. NICHOLS.

The Beilstein[2] test for halogens depending on the green color which copper imparts to a colorless flame in which they are present has been widely used as a sensitive test for halogens and halogen compounds in air and in other gases.   A usual procedure in such cases has been to feed the gas in question into a Bunsen flame in which a spiral copper wire or a copper gauze is suspended.   It has been found that by a careful regulation of the flame as little as one part in a hundred thousand parts of air can be detected in this way.

Of late this method has been widely used, at least in the laboratory, for detecting toxic war gases in air, since they almost invariably contain halogens.   The delicacy mentioned above is adequate for most war gases, but for certain of the more toxic ones, for example, mustard gas, 10- to 100-fold greater delicacy is desirable.   The attempt was therefore made to increase the delicacy of the copper flame test sufficiently to meet these requirements.

This has been accomplished by the very simple expedient of making the test a *cumulative* one.   The air in question is passed over a moderately heated copper spiral or gauze for some time—a longer time the lower the concentration of the halogen.   After this period of accumulation the copper spiral is sharply heated in a suitable flame and the green tinge observed.

Apparatus and Procedure.

The apparatus used in this test is very simple; it consists merely of a quartz tube of about one cm. bore, in which is placed a roll of oxidized copper gauze 50 meshes to the linear inch, 10 to 11 cm. long, wound tightly around a stiff iron wire, which serves as a handle for the insertion and withdrawal of the roll from the tube.   In addition a non-luminous Bunsen or acetylene flame is required.

To carry out a test the air in question is drawn through the tube, while

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[2] Beilstein, *Ber.*, **5**, 620 (1872); Noelting (interference of pyridine), *Ibid.*, **23**, 3664 (1890); W. Lorenz, *Z. anal. Chem.*, **34**, 42 (1895); Erdmann, *J. prakt. Chem.*, (2) **56**, 36 (1897).

the end of the copper roll near the inlet is heated from without to incipient redness. After a suitable period of accumulation the roll is removed from the tube and inserted into a colorless flame. To obtain the best results the copper roll should be introduced not too slowly into the flame, heated end first, the observer watching against a dark background whether any coloration is produced anywhere along the roll. If a non-luminous acetylene flame is used, care must be taken not to melt the copper gauze even superficially, for this results in the production of a green color in the absence of a halogen. After a positive test, by careful heating, all of the green color will usually disappear and the roll is then ready for another test.

Delicacy of the Test. Influence of Different Factors.

To determine the sensitiveness of this test and the influence of different factors such as rate of flow, concentration and temperature upon it, air-halogen mixtures of known concentrations were prepared and the time of accumulation required to give a positive test under different conditions was measured. To obtain with precision the minute concentrations of halogens required, air was passed at a known rate through a saturator containing β-dichloro-diethylsulfide ("mustard gas"), and then mixed in a mixing chamber with a stream of pure air flowing at a known and much more rapid rate. The temperature of the saturator was controlled, and since the vapor pressure of this highly involatile liquid is well known,[1] this gave a known concentration of halogen before dilution in the second air stream. As the rates of flow of the two streams were controlled by delicate valves and were measured by two sensitive flowmeters, the concentration in the dilute gas stream was also accurately known. This arrangement usually provided a more abundant stream of halogen-laden air than was required or was desirable for the test; a mixing chamber was, therefore, provided with an exit opening freely to the hood, and the required amount of mixture as indicated by a third flowmeter was drawn off from the mixing chamber into the quartz testing tube. By this simple means concentrations of chlorine between 0.00003 and 0.003 mg./l., probably accurate to 2 or 3%, were readily secured. A diagram of the whole apparatus is given in Fig. 1.

[1] Vapor Pressure of β-Dichloro-diethylsulfide, and Concentration of its Saturated Vapor.

Temp. ° C.	Vapor pressure. Mm. Hg.	Concentration of vapor.			
		Dichloro-diethylsulfide.		Chlorine.	
		P. P. M.	Mg./L.	P. P. M.	Mg./L.
0.........	0.025	33	0.22	33	0.10
10.........	0.040	53	0.36	53	0.16
15	0.047	62	0.42	62	0.19
20.........	0.062	82	0.54	82	0.24
22.........	0.064	85	0.56	85	0.25
25.........	0.074	98	0.64	98	0.28
30.........	0.090	119	0.76	119	0.34

TABLE I.

Delicacy of Test for Chlorine.

Rate of flow. L./min.	Time of accumulation. Min.	Temp. °C.	Total chlorine. Mmg.	No. of trials.	Minimum chlorine detected. Test.	Mmg.	Remarks.
Approximate Concentration, 0.5 P. P. M., or 1.45 mmg./L.							
1.5	2	25	9.3	4	+		
1.5	1	25	4.7	7	+	4.0	
1.5	1	25	4.7	4	±		Faint
Approximate Concentration, 0.2 P. P. M., or 0.58 mmg./L.							
1.5	4	25	3.5	3	+	2.6	
1.5	3	25	2.7	2	±		Faint
4.0	3	25	7.1	2	+	7.1	
4.0	3	25	7.1	2	—		
8.0	3	25	14.2	4	+	9.3	
8.0	2	25	9.5	2	±		Faint
Approximate Concentration, 0.1 P. P. M., or 0.29 mmg./L.							
1.5	6	23	2.4	2	+		
1.5	6	27	2.8	1	+	2.4	
1.5	5	27	2.3	1	—		
4.0	3	27	3.7	2	+	< 3.7	
8.0	5	28	12.8	1	+		
8.0	5	26	12.0	3	+		
8.0	3	27	7.4	1	+		
8.0	3	26	7.2	1	+	5.5	
8.0	3	22	6.0	3	+		
8.0	2	27	5.0	2	—		
Approximate Concentration, 0.05 P. P. M., or 0.145 mmg./L.							
1.5	20	25	4.4	1	+		
1.5	15	25	3.3	1	+	2.3	
1.5	11	25	2.4	2	+		
1.5	10	25	2.2	2	—		
4.0	11	26	6.6	2	+		
4.0	10	26	6.0	1	+		
4.0	7	26	4.2	2	+	2.8	
4.0	5	28	3.2	1	+		Faint
4.0	5	26	3.0	2	+		Faint
4.0	5	24	2.8	1	±		Faint
4.0	4	24	2.2	2	—		
8.0	11	26	13.2	1	+		
8.0	10	26	12.0	4	+	5.0	
8.0	5	24	5.6	4	+		
8.0	4	24	4.5	2	—		
Approximate Concentration, 0.01 P. P. M., or 0.029 mmg./L.							
4.0	36	27	4.5	1	+		
4.0	25	27	3.1	1	+	2.8	
4.0	20	27	2.5	1	—		
8.0	17	28	4.4	1	+	4.3	
8.0	20	23	4.2	2	—		

The results obtained are collected in Table I.   In this table the concentrations are given both in parts per million by volume (P. P. M.) and in thousandths of a milligram (mmg./l.) per liter, at rates of flow between 1.5 and 8 liters per minute. The temperatures of the dichloro-diethyl-sulfide are recorded and from these data and the known length of the
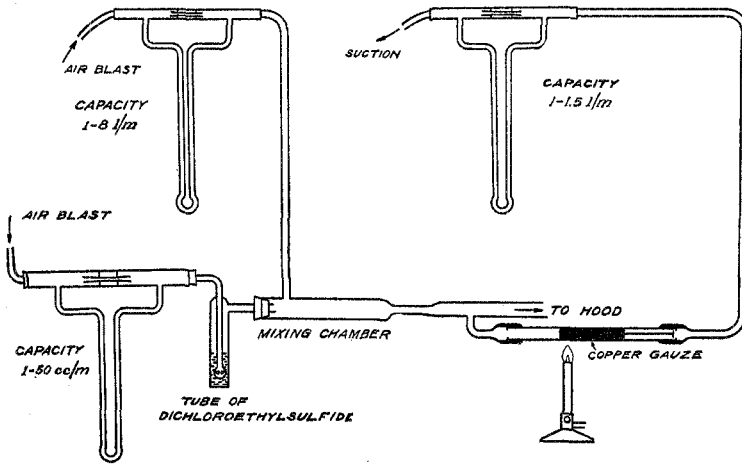

Fig. 1.—Apparatus.

period of accumulation the total chlorine passing over the copper gauze during this period was computed and is given in Col. 4.   The positive or negative test obtained is indicated in Col. 6, respectively by plus and minus signs.   From these results the minimum amounts of chlorine detected, expressed in thousandths of a milligram, are derived and given in Col. 7.

In Fig. 2 these minimum amounts detected are plotted against concentrations at 3 different rates of flow.   This figure indicates that, as would
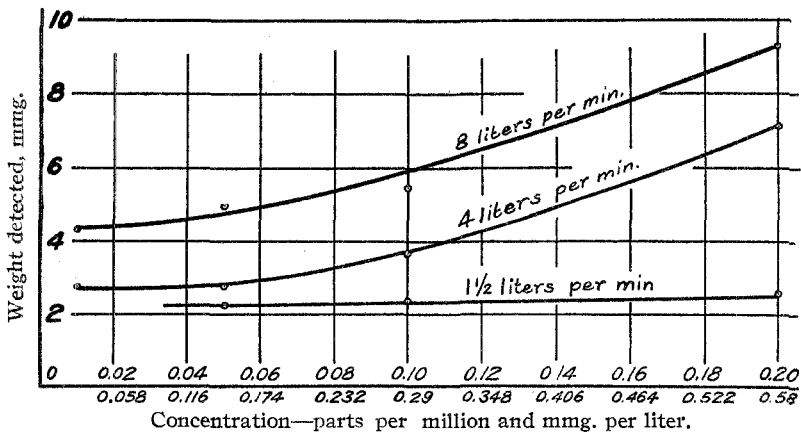

Fig. 2.—Weight of chlorine detected at different concentrations and rates of flow.

be expected, the slower the rate of flow the smaller the absolute amount of chlorine which can be detected. At the slowest rate tried, namely, 1.5 liters per minute, the least amount which could be detected would be 0.0022 mg., and as there is little gain in passing from 4 to 1.5 liters per minute, it is improbable that even by a very much slower rate of flow anything less than 0.002 mg. of chlorine could be detected. This would seem to imply that it requires at least this amount of chlorine to produce a noticeable green color under the above conditions. Fig. 2 further shows that the delicacy at low rates of flow is substantially independent of the concentration, but that at high rates of flow the delicacy is greatest at low concentrations. A simple explanation of this fact would be that beyond a certain critical velocity more or less of the halogen escapes absorption by the copper during the period of accumulation.

Experiments were next made to determine how close a regulation of the temperature of the copper spiral during the period of accumulation was necessary. In the regular procedure followed in securing the above results, the quartz tube was heated to redness on the lower side for 12 to 25 mm., directly underneath the tip of the copper gauze cylinder. A series of duplicate experiments were now run in which the quartz tube was heated much more strongly, namely, to redness for a distance of 38 mm. underneath the end of the copper spiral. Care was taken, nevertheless, to avoid a temperature high enough to volatilize the copper chloride along the entire length of the copper gauze cylinder. No difference could be observed in the sensitiveness of the test under the two conditions.

Duplicate measurements were also made comparing the above copper gauze of 50 meshes to the inch, with a much finer gauze, namely, one of 150 meshes to the inch. A very slight decrease in sensitiveness was observed, presumably due to the increased resistance to the free passage of air through the gauze and hence to the greater tendency for rapid passage of the gas through the larger channels between the copper spiral and the quartz tube. A further objection to the use of the finer mesh was the increased ease with which it melted when slightly superheated, which not only vitiated the results, but produced a deformation of the gauze cylinder, and a consequent increase in leakage.

The "age" of the copper gauzes was, on the other hand, found to be of some importance. A new, bright gauze was found to be less sensitive than one which had been in use for some time. After a number of tests had been made on a gauze no distinction could be observed. This behavior is doubtless due to the formation of a more active surface as the result of the alternate oxidations and reductions incident to the test; indeed, it is very likely connected with the known highly absorbent nature of finely divided copper oxide.[1]

[1] Merton, *J. Chem. Soc.*, **105**, 645 (1914); Brit. pat. 127,609 (1917); U. S. pat. application (1919).

Approximate Estimation of Concentration.

The results obtained proved to be so reproducible that it seemed worth while to determine whether this method could be employed to *estimate* roughly very low concentrations of chlorine and chlorine compounds in air. Evidently, the most convenient way to do this would be first to plot curves, based on the previous results, showing at different rates of flow the periods of accumulation required to give a positive test at different concentrations. This has been done in Fig. 3. Then, in case of an unknown concentration, one need only determine the minimum
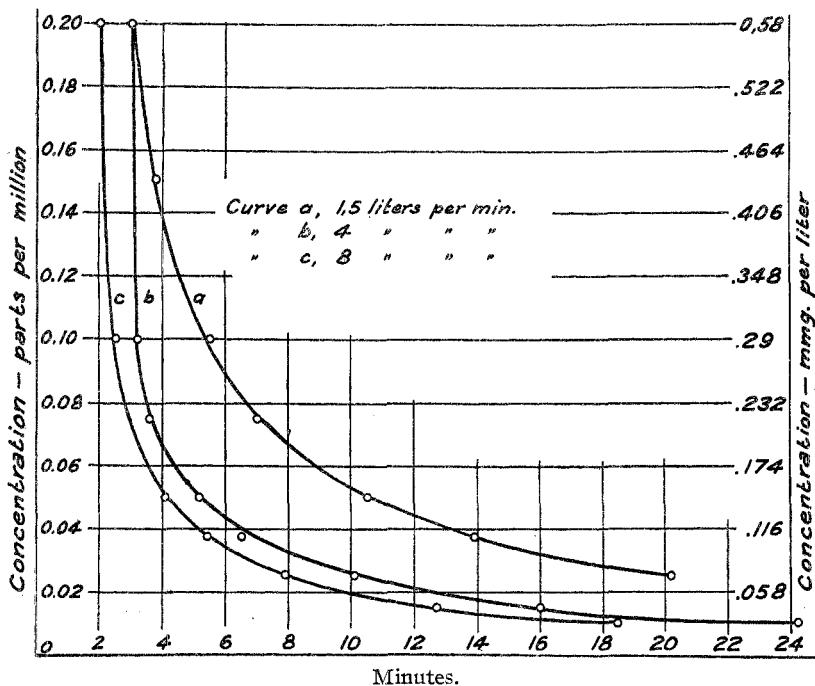

Fig. 3.—Relation between concentration and time of accumulation.

period of accumulation required for a positive test at a given rate of flow and read off from the appropriate curve the concentration which must have prevailed during the period of accumulation. Fig. 3 shows that in general it will be more advantageous to determine relatively high concentrations (0.003 mg./l. and higher) at low rates of flow (1.5 liter per minute); while lower concentrations, because of the long periods of accumulation required, are more conveniently determined at relatively high rates of flow.

To determine the usefulness of this method of approximate analysis, the series of tests given in Table II were carried out at moderate concentrations of halogen (0.15 to 0.29 mmg./l.) corresponding to one part in

twenty and one part in ten million parts of air. By comparison of Cols. 10 and 11 of the table it will be seen that there is a close concordance between the concentrations of the gas mixtures actually used and those predicted by the curve from the times of accumulation required for a positive test.

TABLE II.

Approximate Estimation of Chlorine Compounds in Air.

Rate of flow. L./min.	Temp. °C.	Concentration. P. P. M.	Mmg./L.	Time of accum. Min.	Total chlorine. Mmg.	No. of tests.	Result of tests.	Minimum time for positive test. Min.	Concentration. Actual. Mmg./L.	From curve. Mmg./L
			Approximate Concentration, 0.05 P. P. M.							
1.5	25	0.050	0.147	11	2.4	3	+	10.5	0.15	0.14
1.5	25	0.050	0.147	10	2.2	2	—			
4.0	25	0.050	0.147	7	4.1	2	+	5.2	0.15	0.14
4.0	25	0.050	0.147	5	3.0	5	±			
8.0	25	0.050	0.147	5	5.9	4	+	4.6	0.15	0.14
8.0	26	0.052	0.152	4	4.9	2	—			
			Approximate Concentration, 0.1 P. P. M.							
1.5	24	0.095	0.28	7	2.9	4	+	6.0	0.28	0.27
1.5	24	0.095	0.28	7	2.9	1	—			
1.5	24	0.095	0.28	6	2.5	7	+			
1.5	24	0.095	0.28	6	2.5	2	—			
8.0	24	0.10	0.28	3	7.0	5	+	2.5	0.31	0.29
8.0	28	0.112	0.32	2	5.1	2	—			

As this method depends on the estimation and detection of faint color, it will always require experience and a preliminary calibration, so to speak, of the operator. It would, of course, be possible to arrange for a simultaneous comparison of the air in question with an air mixture containing a known concentration of halogen, but the essentially qualitative nature of the method seemed hardly to justify the additional complexity and difficulty.

Summary.

By the simple expedient of making it cumulative the copper flame test for halogens in air has been rendered much more sensitive, so that as little as one part of halogen in fifty or a hundred million parts of air is readily detected. Moreover, the simplicity and rapidity of the test have not been sacrificed in the process.

The results are sufficiently definite and reproducible to permit a fairly close estimate of the concentration of the halogen from the length of the accumulation period required to give a positive test.

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