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Method of Determination of the Penetration of HS Vapor through Protective Clothing

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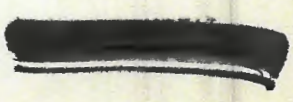
ABSTRACT

This report describes a laboratory method used for measurement of the resistance of impregnated cloth towards penetration by HS vapor. It is not intended to furnish data on the evaluation of any one impregnite. Details concerning the test method as used at this laboratory have been assembled for the information of other investigators, and typical penetration curves are shown and discussed.



AUTHORIZATION

1. This work was authorized under Project #547-41, "Maintenance, Bureau of Ships," dated 16 December 1940. Problems which were proposed for study were given in Bureau of Ships letter S-S77-2 (Dz) Serial 811 of 17 December 1940.

STATEMENT OF PROBLEM

2. This study was undertaken to find a reliable method for determining the efficiency of cloth impregnated with various compounds to destroy HS. A method was desired in which service conditions could be simulated as closely as possible, the effect of high humidity could be studied, and initial penetration concentrations of HS determined.

KNOWN FACTS BEARING ON THE PROBLEM

3. Due to the low vapor pressure of HS and the fact that very low concentrations can produce vesication, HS can exist at dangerous concentrations for long periods of time. This danger may be overcome by the combined use of a gas mask and protective clothing.

4. Methods which have been used in testing the effectiveness of protective clothing are of two general types, the dynamic method used by the Chemical Warfare Service, and a static method used by the British. In the dynamic method as described in E.A.T.R. 278, a stream of dry air containing a known concentration of HS is forced through the cloth under test. The air stream is then passed into an absorber containing 0.004 N potassium dichromate which is decolorized when a certain amount of HS has been absorbed. The British method described in Porton Report 2167 consists in placing the test sample of cloth above a liquid drop of mustard, together with an indicator paper which changes color to indicate the penetration of mustard vapor through the cloth.

THEORETICAL CONSIDERATIONS

5. Any laboratory method of testing the protective power of impregnated clothing must adhere as closely as possible to conditions to be encountered in actual warfare. On the other hand, the laboratory test must be an accelerated one in order to effect a rapid elimination of agents having little or no protective power. The accelerated test is usually accomplished by the use of a greater concentration of HS than normally would be encountered in the field. This is not considered as an unduly accelerated test, however, since high "crash" concentrations will be encountered occasionally.

6. There are certain disadvantages in both the dynamic and static methods as laboratory tests. The dynamic method does not reproduce service conditions in that dry air is used and the air is forced through the cloth. It has been found(1) that when air blows against cloth, as in a strong wind,

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(1) Oral information from Chemical Warfare Service.

only a very small proportion actually penetrates the cloth. Furthermore, the protection given by some impregnites on cloth is known to be affected by the humidity of the air. The British static method suffers from lack of control of humidity and also lack of any quantitative measure of HS penetration. Reliance solely upon diffusion of HS through the cloth may also be objectionable, since this condition would scarcely exist in service.

PREVIOUS WORK AT THIS LABORATORY

7. No previous work has been reported on this problem.

EXPERIMENTAL WORK

8. The method of testing impregnated cloth as developed at this Laboratory is essentially static in that one side of the cloth is exposed to air saturated with HS vapor, while clean air of known humidity is drawn over the opposite side of the cloth. The cloth sample is held in a brass cup as shown in Plate I. A small dish containing liquid HS is placed in the bottom of the cup and saturated HS vapor is maintained against the cloth with a small circulating propeller. The latter is driven by an electric motor at 1700 r.p.m. and it provides gentle but effective circulation. The brass cover contains a baffle which lies 1/4" above the cloth so that the clean air which enters behind the baffle passes over the surface of the cloth and thus sweeps out any HS vapor that has penetrated the cloth. The entire cup assembly is thermostated in an air bath at 30°C to fix the concentration of HS, and the air flow is maintained at 200 ml/min. A water saturator inserted in the air line ahead of the cup allows adjustment of the humidity of the air passing over the cloth.

9. The air from the test cup passes into an absorber containing 0.001 N gold chloride solution. The absorber is of the Vigreaux type modified to permit potentiometric determination of the end point. A simple vacuum tube circuit, described in Section B of the appendix, automatically signals the exhaustion of the gold chloride solution by ringing a buzzer. This permits a saving of time, since the constant attention of the operator is not required. A description of the apparatus and the method of use of the gold chloride indicator along with quantitative studies on known concentrations of HS in air are given in Section A of the appendix. From the length of time necessary to reduce the indicator solution, the average concentration of HS in the air from the test cup is determined.

10. The arrangement described above is adaptable to dynamic tests by providing an inlet tube at the bottom of the cup and inserting a small mustard saturator ahead of the test cup. Due to adsorption of mustard vapor on the walls of the brass cup, reliable results have not yet been obtained by this method, but the protection times determined by the method described in this report may be compared with those obtained by the Chemical Warfare Service. Such comparison with data as given in E.A.T.R. 306 showed that the HS vapor is supplied to the cloth by the present method at a slightly higher rate than by the dynamic method. For example, similar cloths which contained 8% of CC#2 showed a protection time of 200 minutes by the dynamic test, and 160 minutes by the static test described here. Both tests are run at the same temperature, 30°C.

11. The first HS vapor penetration tests were carried out with the use of 0.004 N potassium dichromate in 20% sulfuric acid as an indicator. The end point was difficult to estimate visually, and the quantity of HS required to discharge one bubbler was so great that very few points could be established on a curve to show the rate of penetration against time. The rate at which HS vapor leaks through the cloth initially and the sharpness of the protection break were considered as important in the study of new protective compounds. The use of the gold chloride indicator is advantageous in that a smaller amount of HS can be measured, it is unaffected by hydrochloric acid produced by the reaction of HS with the chloramide, and the end point may be easily and accurately determined.

12. The relative efficiencies of compounds are found by determination of the chloramide remaining on the patch after the HS penetration test and the correlation of this figure with the initial concentration of the chloramide and the protection time obtained. The point which is to be taken as the break time for the cloth should depend on the concentration of HS in air which is to be considered as dangerous in service. A concentration of 0.05 mg HS/liter has been given as vesicant after a 3-hour exposure. Recent work reported by the British has indicated, however, that a concentration of 0.0002 mg HS/liter is definitely irritating. For the laboratory penetration tests, the time at which the concentration in the air stream over the cloth reaches 0.05 mg/liter has been taken as a suitable break point, although the present method makes it possible at any time to read off the protection time corresponding to any predetermined leakage concentration. Small initial penetration of mustard through the cloth may be detected and the effectiveness of impregnating compounds may be studied both as a function of humidity of the air and of concentration of HS.

13. A large number of runs has indicated that the results now being obtained are reliable. The type of penetration curves which result are illustrated in Plates 9 and 10, Appendix A. Test data are being accumulated on the more promising compounds, based on the standard method of impregnation now being used in the service, and these will be reported along with other data on the effect of weathering on both the chloramide and the cloth.

SUMMARY AND CONCLUSIONS

14. A laboratory method for determination of the penetration of HS vapor through permeable cloth has been developed which permits a variation of humidity of the air as well as HS vapor concentration, and which simulates service conditions as closely as possible.

15. Quantitative studies on the use of the gold chloride indicator against known concentrations of HS vapor in air have made possible more accurate data on its penetration through cloth and a reliable comparison of the efficiency of various impregnites. The apparatus and method may also be used to study the penetration of HS through non-permeable protective materials such as oiled silk and synthetic films.

APPENDIX A

The Use of Gold Chloride for the Determination of HS in Air

1. The use of gold chloride as an indicator for mustard gas has long been recognized, since this reagent forms an insoluble addition compound detected visually as a cloudiness. At temperatures in the neighborhood of 80°C, gold chloride reacts with HS to form metallic gold, so that any addition compound exists only momentarily. Under certain conditions, the metallic gold occurs as a highly colored colloidal sol which greatly aids in visual detection. In view of the fact that any gases having a similar reducing action will affect the gold chloride, this reagent cannot be designated as specific for HS.

Apparatus and Method

2. Various known concentrations of HS in air were obtained from solutions of HS in dibutyl phthalate. Dibutyl phthalate was chosen as the solvent because it has a very low vapor pressure, is relatively stable, and because preliminary tests showed that an air stream passed through it did not affect the gold chloride reagent. The saturator containing the HS solutions was of the air-lift type and was maintained in a thermostat at 30°C. In Table 1 the composition of the solutions is given together with the corresponding concentrations of HS in air calculated from Raoult's Law. In view of the fact that deviations from Raoult's Law were to be expected, especially at the higher concentrations, it was necessary to determine analytically the actual concentration of HS in air passed through each solution. The air stream from the saturator was passed through three absorbers of the Vigreaux type connected in series with ground glass joints and each containing 5 ml of 20% acetic acid. Dried air was passed into the system at the rate of 200 ml/min. for a measured time. The contents of the three absorbers were removed quantitatively and the chloride resulting from hydrolysis of the HS was titrated potentiometrically with 0.001 N silver nitrate. It was necessary to keep the total volume as small as possible in order to maintain a sharp end point. In every case, approximately 90% of the chlorine was found in the first absorber, 10% in the second, and none in the third. Blanks were run on the acetic acid solution. A sketch of the titration cell is shown in Plate 2, and the results of the analyses for HS are given in Table 1. The potential measurements were made with a Rubicon portable potentiometer using a small L&N light-in-box galvanometer.

Table 1

Analysis of HS - Air Mixtures
for Conc. of HS

gr. HS	gr. Dibutyl Phthalate	(mg/l.) Conc. HS in Air (Calc.)	Flow Rate ml/min.	Time (min.)	ml. 0.00102 N $AgNO_3$ 1st Bubbler	2nd Bubbler	Total	Conc. HS in Air (mg/l.) (Found)
2.0210	50.00	0.0954	200	20	3.80	0.35	4.15	0.0804
			200	25	4.70	0.25	4.95	0.0804
			200	60	5.60	0.40	6.00	0.0410
			200	50	4.85	0.40	5.25	0.0426
1.0313	50.25	0.0500	200	45	4.40	0.30	4.70	0.0424
			200	45	4.35	0.35	4.70	0.0424
			200	45	4.40	0.35	4.75	0.0428
0.5367	50.10	0.0266	200	80	4.10	0.35	4.45	0.0226
			200	70	3.70	0.40	4.10	0.0228
0.2508	50.40	0.0125	200	140	3.30	0.20	3.50	0.0102
			200	150	3.55	0.40	3.95	0.0107
0.1254	50.20	0.0063	200	285.5	3.45	0.25	3.70	0.0052

3. Two types of HS absorbers were found satisfactory for use on the gold chloride solution. The modified Vigreaux type shown in Plate 3 was used in most of the experiments described here. The second absorber differed only in that a solid glass spiral replaced the indentations in the outer wall of the absorber. The most important feature of these absorbers was their construction so as to form a titration cell in which the end point of the reaction between the gold chloride and HS was determined potentiometrically. The following description of procedure will illustrate the use of the absorber. A small amount of saturated potassium sulfate solution was admitted to the bottom of the absorber from the reservoir which contained a calomel half cell. 5 mm of 0.001 N gold chloride solution were allowed to run into the absorber from the calibrated reservoir. When the air flow of 200 ml/min. was started, the liquid level was raised sufficiently to contact the gold-plated platinum electrode and thus complete the electrical circuit comprising the cell.

4. The cell voltage was measured at intervals with a potentiometer, or continuously by means of a suitable voltmeter. A circuit tester such as the RCA Voltohmyst, Jr. has been found satisfactory. The large voltage drop at the end point permitted the use of a simple vacuum tube circuit to operate a relay, which in turn actuated a buzzer and stopped the timer. The circuit is shown in Appendix B. After the end point was reached the cell was drained, rinsed, and refilled for the next run. The gold chloride used for the indicator was made up to 0.01 N from Merck Reagent Grade $HAuCl_4 \cdot 3H_2O$. The 0.001 N

solutions were made up from stock solution as needed, since they are not stable over long periods of time. The pH of the 0.001 N solution was approximately 3.0, and determination of the pH of the solution at the end point showed no measurable change from this value. It was found that buffered solutions having a pH of 2.5 gave a less sharp end point, while at a pH of 4.5 or above, no end point was obtained at all. The exact concentration of the solution was determined by potentiometric titration using potassium iodide and standard thiosulfate solution. After the addition of 5 ml of 10% KI to 5 ml of the gold chloride solution, the liberated iodine was titrated with 0.001 N thiosulfate solution.

5. Experiments carried out with the gold chloride absorber maintained at 70° and 90°C showed only a small variation. The temperature of the bath was maintained at 80 ± 2°C. At 70°C the potential drop of the end point was less sharp.

Experimental Data

6. Preliminary experiments showed that the gold chloride solutions were not destroyed after 16 hours in blank runs, but for quantitative studies it was necessary to measure any decomposition which did occur. Clean air was passed at the standard rate through the solutions kept at 80°C. The results given in Table 2 and shown graphically in Plate 4 show that some decomposition occurs rapidly at first. In Plate 5 a comparison is shown of the decomposition of the 0.001 N gold chloride and 0.004 N potassium dichromate.

Table 2

Stability of 0.001 N $HAuCl_4$

	Time (hrs.)	Normality	% Decomposition
	0.0	0.00100	0.0
	0.25	0.00091	9.0
	0.50	0.00087	13.0
Curve #1	1.00	0.00086	14.0
	2.00	0.00084	16.0
	4.00	0.00083	17.0

7. Results of the experiments carried out to determine the equivalence of the gold chloride against HS at different concentrations of HS are given in Table 3. Similar experiments for the dichromate solution are shown in Table 4. In the calculation of the equivalence values, a correction was applied for the decomposition of the indicator solutions during a run. This correction is not strictly valid, since it is not known if the decomposition occurs at the same rate in the presence of HS. The decomposition should also decrease as the concentration of gold chloride remaining in the solution decreases. For use in the actual penetration studies, however, no such difficulty is encountered since the concentration of HS in the air stream is obtained from the experimentally determined curve.

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Table 3

Stoichiometric Data
HS - $HAuCl_4$
Flow Rate - 200 ml/min.

Conc. of HS in Air (mg/l)	Time for Reduction of 5 ml of 0.00102 N $HAuCl_4$ (min.)		Mg Hs equiv. to 5 ml 0.00102 N $HAuCl_4$ (corrected)	Valence Change of HS
0.0804	13.8 13.9 14.6 13.8	14.0	0.228	3.5 ± 0.2
0.0422	24.1 22.3 23.7	23.4	0.220	3.6 ± 0.2
0.0227	39.2 41.3 40.9 38.2	40.2	0.191	4.2 ± 0.2
0.0104	73.6 71.5 77.4	74.1	0.161	4.9 ± 0.2
0.0052		143.4	0.159	5.0

Table 4

Stoichiometric Data
HS - $K_2Cr_2O_7$
Flow Rate - 200 ml/min.

Conc. HS (mg/l.)	Time of Test (min.)		Mg HS for 5 ml. 0.004 N $K_2Cr_2O_7$	Valence Change of HS
0.0192	174.9 150.3 153.2	159.5	0.632	5.0 ± 0.5
0.0422	83.9 87.8	85.9	0.762	4.2 ± 0.1
0.0807	55.9 55.8	55.9	0.926	3.4 ± 0.0

8. The oxidation of HS or thiodiglycol resulting from hydrolysis would be expected to proceed with the formation of the sulfoxide or sulfone. Potentiometric titration of HS solutions with 0.004 N potassium dichromate in 20% H_2SO_4 showed that the reaction was closely equivalent to formation of the sulfoxide. This was not true, however, for HS removed from an air stream by the absorbers. The observed change in equivalence with concentration of HS indicated that no single clean-cut reaction occurred. With low concentrations of HS passing into the absorber, there was sufficient time before the end point was reached for some further slow oxidation of the molecule to take place. It was known that this slow reaction in the case of the dichromate solution included the oxidation of chloride ion from the HS, since the dichromate in the presence of a small excess of chloride was completely reduced at 80°C in about two hours. The possible evolution of HCl from the impregnated cloth being tested would introduce uncertainty into any leakage concentration of HS determined with the dichromate indicator. Plates 6 and 7 show the change of equivalence against mustard for the gold chloride and dichromate, respectively. In Plate 8 the reduction times for the gold chloride indicator are plotted against a concentration of HS in the air stream. By the use of this curve the bubbler times obtained in penetration tests may be converted to a concentration of HS in the air stream from the test cup. This gives an average concentration for the period required to discharge the gold chloride solution. The use of this concentration-time plot in evaluating protective cloth is illustrated in Plates 9 and 10. From the length of time required for the discharge of a series of bubblers, a plot is made of the rate of penetration of HS through the cloth as a function of time. In Plate 10, the peculiar behavior of one impregnating agent is shown to illustrate the usefulness of this type of curve in the comparison of new compounds.

9. A study of the equivalence of the gold chloride against HS as a function of gold chloride concentration also revealed some variation. In this case the change was not much greater than the experimental error. The results obtained in this study are given in Table 5.

[redacted]

Table 5

Stoichiometric Data

$HS - AuCl_4$

Flow Rate - 200 ml/min.; Conc. of HS - .042 mg/l.

Normality of $HAuCl_4$ (Corrected)	Time for reduction of 5 ml. of $HAuCl_4$ (min.)		Mg HS equiv. to 5 ml. $HAuCl_4$	Valence Change of HS
0.00492	145.3 136.1	140.7	1.170	3.3 ± 0.1
0.00202	58.6 50.3 52.1	53.6	0.451	3.5 ± 0.2
0.00089	24.1 22.3 23.6	23.3	0.196	3.6 ± 0.2
0.00049	13.0 12.0 11.5 14.3	12.7	0.105	3.8 ± 0.4

10. Mention should be made of observations on the color produced in the gold chloride solutions. It was found to be unreliable for quantitative measurements. Frequently no color developed during an experiment, and at a concentration higher than 0.001 N gold chloride no color was produced. In general the first color observed was a light blue, probably due to the presence of electrolyte from the salt bridge. This gradually changed to pink as more gold was reduced. A comparison of the time required for the development of a pink color and the actual potentiometric end point revealed that the former occurred at about 70% of the time required for complete reduction. In the absence of the salt bridge, the formation of color was more dependable but not as accurate as the potentiometric determination. The sharp end point and large potential drop observed with the gold chloride solution are shown by a typical curve in Plate 11. Plate 12 shows a similar curve for the dichromate solution.

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APPENDIX B

Automatic End Point Detector

1. The large potential drop at the end point for the gold chloride reagent lends itself to use of the automatic end point detector shown in Plate 13. In principle, the circuit is very simple.

2. The potential developed by the gold chloride cell is applied as part of the grid bias on a 6J7 tube, which acts as a voltage amplifier. As the potential of the gold chloride cell drops, the plate current of the 6J7 tube decreases and thereby reduces the voltage drop across the plate resistor.

3. The voltage drop of the 6J7 plate resistor in turn controls the bias of a gas discharge tube, type 884. In the plate circuit of the 884 is a small relay which contacts a buzzer and electric clock. The circuit is set so that the end point potential of the gold chloride cell just causes the gas tube to fire, ring the buzzer and stop the clock. Any potential greater than the end point potential prevents the firing of the gas discharge tube.

4. Adjustment is obtained by replacing the gold chloride cell with a battery supplying the exact end point voltage and varying the fixed bias until the gas tube fires. No trouble has been encountered with this simple circuit in the course of several months' continuous use.