NOTE.

Correction.—The diagram on page 70 of the January, 1920, Journal was inverted. The correct orientation is shown herewith.

H. W. Foote.

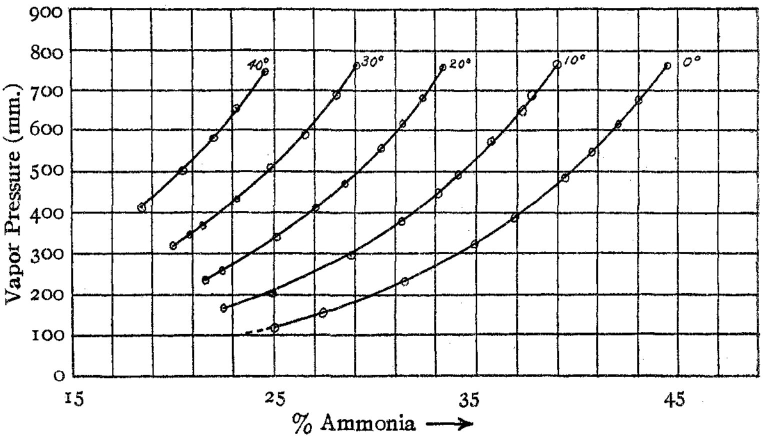

Fig. 1.

[Contribution from the Gas Mask Research Section, Chemical Warfare Service, U. S. A.]

QUANTITATIVE DETERMINATION OF TRACES OF DICHLORO-ETHYLSULFIDE (MUSTARD GAS) IN AIR.[1]

By Max Yablick, G. St. J. Perrott and N. H. Furman.

Received March 19, 1919.

A Nephelometric Method Using Selenious Acid.

This paper deals with a very sensitive method for analyzing air mixtures containing traces of dichloro-ethylsulfide. The method was developed as the result of a need for a qualitative test for mustard gas which should indicate the presence of dangerous amounts of the substance in the air. When it is known that concentrations of the vapor as low as 0.0005 mg. per liter (0.08 p. p. m.) will cause discomfort on exposure for 25 minutes and concentrations between 0.001 mg. per liter and 0.005 mg. per liter (0.2 p. p. m. and 0.8 p. p. m.) will cause skin burns if exposure is as long as 30 minutes, it can be seen that an extremely delicate indicator is necessary to vie in sensitivity with the physiological test.

Briefly, the method consists in reducing a 1% solution of selenious acid in 1 : 1 sulfuric acid by means of the dichloro-ethylsulfide vapor to an orange-red suspension of selenium, the solution being heated to about 85° to facilitate the reaction. In this way amounts of the substance as low as 0.005 mg. can be detected.

[1] Approved for publication by the Director of the Chemical Warfare Service.

The amount of the suspension produced is nearly directly proportional to the amount of dichloro-ethylsulfide present. Amounts of the compound from 0.10 mg. to 0.01 mg. can be estimated with a fair degree of accuracy by nephelometry.

The method has had a variety of uses, among which may be mentioned the detection of the presence of mustard gas in field and factory, securing of quantitative data as to the persistency of the gas over contaminated soil, and determining the permeability of protective fabrics to the vapor and liquid.

Schulze[1] first prepared a hydrosol of selenium in 1885 by reduction of a solution of selenious acid with sulfurous acid ($1SeO_2 : 2SO_2$)

$$H_2SeO_3 + 2H_2SO_3 = 2H_2SO_4 + H_2O + Se$$

With changed proportions, reduction is incomplete. When an excess of sulfur dioxide is present $H_2SeS_2O_6$ is formed, with excess of selenium dioxide $H_2Se_2SO_6$ is formed. The reaction takes place more completely in the presence of hydrochloric acid. Hydroxylamine and hydrazine salts also reduce selenious acid with precipitation of metallic selenium.[2] Glucose, formic acid, formaldehyde and a number of organic acids and aldehydes have been found to have a similar action.[3]

We have not investigated the mechanism of the reduction of our selenious acid reagent by dichloro-ethylsulfide. A possible explanation is that the nascent sulfur dioxide set free by the reaction between warm sulfuric acid and dichloro-ethylsulfide effects the reduction. The decomposition products of the dichloro-ethylsulfide may possibly play some part in the reaction.

Apparatus and Solutions Used.

In our work the nephelometric comparison method described by Kober has been employed.[4] A nephelometer colorimeter made by the Klett Manufacturing Co., New York City, was used.

In order to estimate the strength of suspensions produced by unknown amounts of vapor it was necessary to devise some means of preparing reproducible standard suspensions equivalent to known amounts of the vapor. For this purpose standard solutions of dichloro-ethylsulfide were prepared as follows: I. A stock solution made by dissolving about 0.01 g. dichloro-ethylsulfide in 100 cc. of cold 1 : 1 (by volume) sulfuric acid; II. For use, 10 cc. of Solution I was diluted to 100 cc. with cold 1 : 1 sulfuric acid. This solution was found to remain unchanged for several weeks.

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[1] H. Schulze, *J. prakt. Chem.*, [2] 32, 390–407 (1885).

[2] Jannasch and Müller, *Ber.*, 31, 2388 (1898).

[3] Oechsner, de Coninck and Chauvenet, *Compt. rend.*, 141, 1234 (1905).

[4] *J. Ind. Eng. Chem.*, 10, 556–63 (1918).

The selenious acid reagent contained 1.0 g. of selenium dioxide per 100 cc. of cold 1 : 1 sulfuric acid.

The solutions of dichloro-ethylsulfide were used to prepare standard suspensions of selenium corresponding to a suitable range of weights of dichloro-ethylsulfide per 20 cc. of the suspension medium which was 1 : 1 sulfuric acid.

Procedure in Use of Nephelometer and Method for Obtaining a Standard Curve.

In preparing the nephelometric curve shown in Fig. 1, suitable amounts of Solution II were pipetted out so that the selenium suspensions corresponded to 2, 1.5, 0.9, 0.8, etc., times the value of the standard. The standard suspension corresponded to 0.045 mg. of dichloro-ethylsulfide per 20 cc.

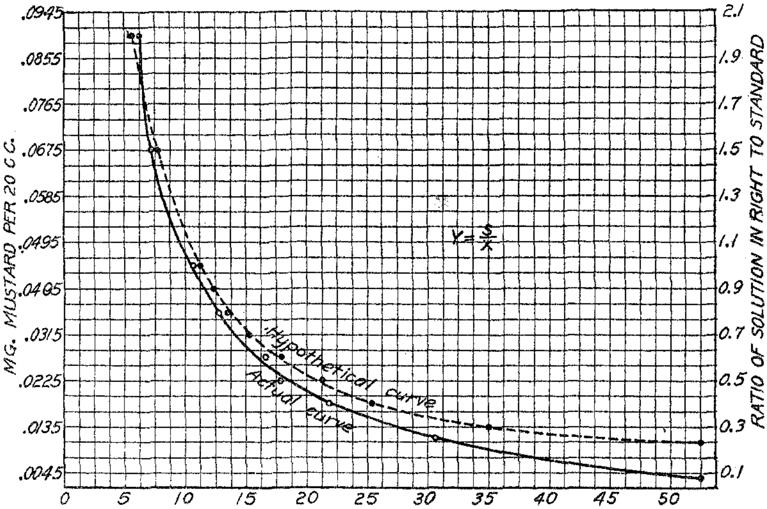

Fig. 1.

The method of preparing the standard and other suspensions may be illustrated from the following data.

Dichloro-ethylsulfide Solution I contained 0.0078 g. per 100 cc. Dichloro-ethylsulfide Solution II contained 0.00078 g. per 100 cc. Therefore, 5.8 cc. of Solution II contained 0.045 mg. of dichloro-ethylsulfide. To 5.8 cc. of dichloro-ethylsulfide Solution II were added 4.2 cc. of 1 : 1 sulfuric aicd and 10 cc. of selenious acid reagent. The resulting mixture was agitated until uniform. It was then maintained at 85° ± 5° for 10 minutes, and cooled to room temperature.

The resulting selenium suspension was then placed in both cups of the nephelometer, the left-hand platform being set at 10 mm. The reading of the right-hand platform was taken after adjusting the height of the column of liquid until equal intensity of illumination was obtained in both fields of the eyepiece.

In the right-hand cups were then placed suspensions containing 2.0, 1.9, 1.5, etc., 0.9, 0.8, etc., times as much dichloro-ethylsulfide per 20 cc. as the standard contained, the respective readings being noted.

In each case the cup was rinsed with 3 portions of the solution to be tested, and the outside of the cup washed with distilled water and dried before the readings were taken.

In Fig. 1 is a curve obtained by plotting the mean of readings taken on different days, and upon standards made from several different dichloro-ethylsulfide solutions. The hypothetical curve is based on the assumption that the scale reading varies inversely as the amount of suspended material present.

The close proximity of the two curves indicates that the reaction between selenious acid and dichloro-ethylsulfide is very nearly complete under the conditions outlined.

A few results will serve to show the consistency of the readings.

Date.	Dichloro-ethylsulfide solution.	Ratio of standard solution to solution in right.		
		1 : 1.	1 : 0.5.	1 : 0.2.
July 25	A	11.1	17.8	30.5
July 26	A	10.7	..	..
July 29	B	10.3	..	..
		11.3	17.5	33.0
July 30	B	10.9	17.2	32.0
Aug. 8	C	10.0	17.0	33.0
Aug. 12	D	10.7	16.0	30.0
Aug. 14	D	10.5	17.0	..

Solutions were prepared by one observer, in a manner similar to that in which the solutions mentioned above were made, and the readings were taken by another observer.

	Dichloro-ethylsulfide taken. Mg.	Dichloro-ethylsulfide found. Mg.	Error. Mg
1	0.0450	0.0428	−0.0022
2	0.0312	0.0347	+0.0035
3	0.0234	0.0243	+0.0009
4	0.0150	0.0170	+0.0020
5	0.0078	0.0079	+0.0001

After the foregoing method for determining the strength of solutions of dichloro-ethylsulfide had been worked out, our attention was turned to the question of estimating amounts of the vapor present in air-dichloro-ethylsulfide mixtures and to find insofar as our limited time allowed the optimum conditions for absorption which should best combine sensitivity and reproducibility.

Factors Affecting Accuracy of Method.

Several series of experiments were run, first to determine the reproducibility of the standard method using a 1% solution of selenium dioxide in 1 : 1 sulfuric acid; second, to determine the effect of varying the amount of sulfuric acid in the cold absorbing solution; third, to find the effect of varying the strength of an aqueous solution of selenium dioxide; fourth, to determine the stability of the selenious acid solution and of the dichloro-ethylsulfide solution used in preparing standard suspensions. Unavoidable circumstances have prevented our making the investigation complete. We are able to say, however, that we have developed a quantitative method for determining amounts of dichloro-ethylsulfide in air from 0.1 mg. to 0.01 mg. with a maximum error of about 0.005 mg.

Apparatus Used in Producing Low Concentration of Dichloro-ethylsulfide Vapor.

The apparatus shown in the figure was arranged to deliver one liter per minute of an air mixture containing about one part per million of dichloro-ethylsulfide.

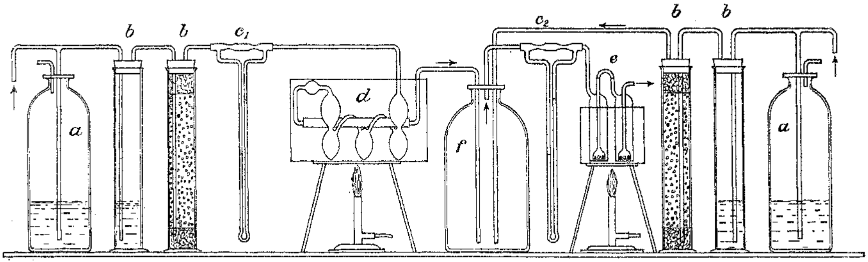

Fig. 2.

a.—constant pressure bottle.
b.—air-purifying bottle.
c.—flow meter.
d.—mustard bubbler in bath at 20°.
e.—selenious acid bubbler in bath at 85°.
f.—mixing jar.

The bulb D contains dichloro-ethylsulfide redistilled *in vacuo* and is kept in a water bath at 20°. Air purified by passing through sulfuric acid and a charcoal, soda-lime mixture is passed through the liquid in bulb D at a rate of 11 cc. per minute as measured by the flowmeter C.[1] The saturated air passes into the mixing chamber F where it is mixed with pure air sufficient to bring the entire flow up to 1000 cc. per minute as measured by the flowmeter C_2. The air mixture, containing 0.0062 ± 0.0004 mg. per liter,[2] now passes through the absorbing solution in the bubblers E.

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[1] Rates and concentrations varying slightly from this figure were used in several determinations described later.

[2] Calculated from British data on vapor pressure of dichloro-ethylsulfide.

Treatment of Absorbing Solutions.

Ten cc. of the absorbing agent used is placed in the bubbler and the mixture passed through it for 10 minutes. Ten cc. of a solution of selenious acid in sulfuric acid is then added, the sulfuric acid being of such strength as to make the resulting mixture 1:1 sulfuric acid and the selenious acid present in the same per cent. as in the original 10 cc. of absorbing agent; for example, if 10 cc. of a 1% solution of selenium dioxide in water were used as the absorbing medium, then 10 cc. of a 1% solution of selenium dioxide in conc. sulfuric acid is added making 20 cc. of a 1% solution of selenium dioxide in 1:1 sulfuric acid.

The solution is then heated for 10 minutes in a bath at 85°, cooled, and the strength estimated by comparison with a standard solution prepared as previously described. Data are given in terms of milligrams per liter, *i. e.*, 1/10 of the actual amount of dichloro-ethylsulfide measured.

1. Using a solution of 1% selenium dioxide in 1:1 sulfuric acid, to find the effect of passing the vapor through the hot and cold solution.

Hot solution, mg./liter.	Deviation from mean.	Hot solution, mg./liter.	Deviation from mean.
0.0063	+0.0001	0.0056	—0.0003
0.0062	—0.0000	0.0061	—0.0002
0.0067	+0.0005	0.0053	—0.0006
0.0058	—0.0004	0.0063	+0.0004
0.0060	—0.0002	0.0058	—0.0001
0.0063	+0.0001	0.0060	+0.0001
0.0065	+0.0003	0.0062	+0.0003
Av., 0.0062	0.0002	0.0059	0.0003

Solutions heated 10 min. at 85° before taking nephelometric readings.

Amount actually present as calculated from vapor-pressure measurement = 0.0062 ± 0.0004.

From the above data it is evident that there is no apparent difference between results when hot and cold selenious sulfuric acid solutions are used as absorbents.

2. To find the effect of varying the amount of sulfuric acid in *cold* selenious sulfuric acid solution.

Results show less deviation from the mean and more closely approach the theoretical, when sulfuric acid is present in the original absorbing solution.

3. To find the effect of increasing the strength of a water solution of selenium dioxide.

It had been noticed in a qualitative way that very concentrated water solutions of selenium dioxide gave a heavier precipitate for an equal amount of dichloro-ethylsulfide than did dilute solutions. To find the magnitude of this change in sensitivity, a concentration of 0.0062 mg. per liter of dichloro-ethylsulfide was passed through water solutions

1% SeO_2 in conc. H_2SO_4, mg./liter.	Deviation from mean.	1% SeO_2 in 1 : 1 H_2SO_4, mg./liter.	Deviation from mean.	1% SeO_2 in H_2O, mg./liter.	Deviation from mean.
0.0058	+0.0004	0.0053	—0.0005	0.0063	—0.0010
0.0051	—0.0003	0.0060	+0.0002	0.0081	+0.0008
0.0053	—0.0001	0.0068	+0.0010	0.0077	+0.0004
0.0061	+0.0007	0.0057	—0.0001	0.0069	—0.0004
0.0060	+0.0006	0.0059	+0.0001	0.0091	+0.0018
0.0059	+0.0005	0.0055	—0.0003	0.0068	—0.0005
0.0047	—0.0007	0.0062	+0.0004	0.0074	+0.0001
0.0048	—0.0006	0.0061	+0.0003	0.0082	+0.0009
0.0053	—0.0001	0.0060	+0.0002	0.0065	—0.0008
0.0050	—0.0004	0.0054	—0.0004	0.0063	—0.0010
Av., 0.0054	0.0004	0.0058	0.0004	0.0073	0.0008

Amount actually present calculated from vapor-pressure measurements = 0.0062 ± 0.0004.

NOTE.—The solutions after absorbing the vapor were made to contain 1:1 H_2SO_4, heated for 10 minutes at 85° and cooled before being read with the nephelometer.

of different strengths of selenious acid for 10 minutes and the resulting solution developed as before and estimated in comparison with a standard suspension made from a 1% selenious acid solution. In this way we obtained figures indicating the relative amounts of suspension produced in various strength solutions by a constant quantity of dichloro-ethylsulfide. Experiments were run both with the solution hot and cold during absorption. Each result is the average of 5 determinations.

0.0062 mg./liter present.

% SeO_2.	Amount found.			
	Solution, hot, mg./liter.	Error.	Solution, cold, mg./liter.	Error.
10.00	0.0380	+0.0318	0.0072	+0.0010
5.00	0.0213	+0.0151	0.0078	+0.0016
4.00	0.0184	+0.0122	0.0079	+0.0017
3.00	0.0130	+0.0068	0.0074	+0.0012
2.00	0.0093	+0.0031	0.0069	+0.0007
1.00	0.0067	+0.0005	0.0064	+0.0002
0.50	0.0033	—0.0029	0.0053	—0.0009
0.25	0.0014	—0.0048	0.0049	—0.0013
0.125	0.0012	—0.0050	0.0027	—0.0035

Results show that a very large increase in sensitivity is obtained by using a concentrated hot solution of selenium dioxide in water. The 10% solution gives about 10 times as dense a suspension as is obtained by the method first described where a 1% solution of selenium dioxide in 1:1 sulfuric acid is employed. Results at these high percentages, however, are very erratic and cannot be duplicated to within 50%, and in general results using aqueous solutions as absorbents are not duplicable with any degree of accuracy. Using a cold aqueous solution, the difference is very much less marked, the 10% solution giving only about 1.3 greater density of suspension than the standard.

4. Aging of the selenious acid solution.

1% SeO_2 in 1:1 H_2SO_4 in each case 0.055 mg. of dichloro-ethylsulfide was actually present.

Date of test.	Solution made Oct. 24. Mg.	Solution made Oct. 16. Mg.
Oct. 24	0.038	0.053
Oct. 25	0.057	0.059
Oct. 28	0.058	0.057
Oct. 29	0.055	0.053
Oct. 30	0.055	0.052

This series of results was obtained by passing air-dichloro-ethylsulfide mixture from the standard machine through 20 cc. of selenium acid solution contained in the bubbler and kept in a bath at 85°. Each figure is the average of 5 determinations.

Data show that the selenious acid solution should not be used until 24 hours after it is made up, but that after this time the solution is stable for at least two weeks.

5. Aging of standard solution of dichloro-ethylsulfide.

A standard solution of dichloro-ethylsulfide was made up as previously described. This was tested at intervals of one week by comparison with a suspension of selenium made by passing 0.045 mg. of dichloro-ethylsulfide vapor into 20 cc. of selenious acid reagent as previously set forth. This was then compared with a suspension made by adding an amount of the standard solution containing 0.045 g. of dichloro-ethylsulfide to 10 cc. of the selenious acid reagent and making the whole up to 20 cc. with 1:1 sulfuric acid. The same procedure was carried out with a standard solution made up the same day. Each figure is an average of 5 determinations.

Age of standard. Weeks.	Amount found. Mg.	Amount found, using freshly made standard. Mg.
1	0.046	0.046
2	0.045	0.045
3	0.042	0.046
4	0.046	0.044

Variations are within the experimental error of the method. Apparently little deterioration of the standard solution takes place over a period of 4 weeks.

Discussion.

The temperature at which the solution is heated in process of "developing" can vary 5° in either direction without affecting the character of the suspension. The method is remarkably free from the necessity for extreme purity of original solutions, cleanliness of glassware, etc., which obtains in silver halide nephelometry.

Attempts to determine the strength of the suspension colorimetrically were not successful.

It was not found possible to use good solvents for dichloro-ethylsulfide as absorbing solutions and then determine the strength by our method, for the reason that the only suitable solvents (alcohol and acetic acid) reduced the selenious acid to some extent.

The selenious acid reagent is not specific to mustard gas. Arsine and the substituted arsines and several other toxic gases react with it vigorously.

Selenious acid may have a possible use as an indicator in oxidation-reduction reactions.

We wish to express our appreciation of the work of A. E. Plumb, who made a great many of the determinations.

Summary.

A solution of selenious acid in 1 : 1 sulfuric acid is reduced by traces of dichloro-ethylsulfide giving an orange-red suspension of selenium. About 0.005 mg. of dichloro-ethylsulfide can be detected in this manner. A nephelometric procedure for determining amounts of the substance between 0.1 mg. and 0.01 mg. with a maximum error of 0.005 mg. has been developed.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC COMPANY.]

THE OCTET THEORY OF VALENCE AND ITS APPLICATIONS WITH SPECIAL REFERENCE TO ORGANIC NITROGEN COMPOUNDS.

BY IRVING LANGMUIR.

Received July 7, 1919.

The octet theory of valence[1] leads to structural formulas for organic compounds which are identical with those given by the ordinary valence theory whenever we can assume a valence of 4 for carbon, 3 for nitrogen, 2 for oxygen and one for hydrogen and chlorine. This follows from the following reasoning:

Let us represent by E the number of electrons in the shell of an atom. For the elements of the two short periods E is equal to the ordinal number of the group in the periodic system. Thus for hydrogen and sodium $E = 1$, for carbon $E = 4$, for nitrogen and phosphorus $E = 5$, for oxygen and sulfur $E = 6$ and for chlorine $E = 7$.

We represent by e the total number of electrons in the shells of the atoms that combine to form a molecule. Let n be the number of octets formed

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[1] G. N. Lewis, THIS JOURNAL, 38, 762 (1916); Langmuir, *Ibid.*, 41, 868, 1543 (1919); and *Proc. Nat. Acad. Sci.*, 5, 252 (1919).