

experience. It may seem illogical in view of the fact that charcoal plate is quite generally agreed to have practically as numerous pinholes in the tin coat as coke plate, as revealed by the gelatin test. It suggests the conclusion that these pinholes are at least a minor source of corrosion. The question may then be asked—in what way does a heavier coating of tin function to give added protection against corrosion? To view the corrosion in tin cans as entirely governed by the electric couple set up between the tin and any exposed iron is an inadequate visualization of all the facts. It would seem that one such couple would be as effective as many in perforating the can.

A possible explanation of the added protection afforded by a heavier tin coating may be found in its lubricating effect in can manufacture. There is no doubt that the weakest points in cans are where the metal is subjected to a strain

either in the various forming processes or at points where the can received dents due to rough handling. In making cans from untinned sheets it was found that there was a much greater tendency to fracture than is the case with tin plate, and added lubricant was necessary. This suggests that the tin does function as a lubricant and it is known that the draw of tin plate is influenced by the weight of the tin coat. A heavier coating may be beneficial largely in giving a more uniform draw and a less strained base plate. Such a function of tin in tin plate has received too little attention.

Acknowledgment

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Selenium Sulfide—A New Detector for Mercury Vapor¹

By Birger W. Nordlander

GENERAL ELECTRIC COMPANY, SCHENECTADY, N. Y.

THE detection and measurement of traces of mercury vapor, the poisonous effect of which is well known, have recently assumed considerable importance by reason of the increasing use of the metal in industrial processes, such as the mercury boiler, heating operations, and various catalytic applications.

Most of the methods employed by previous investigators for the determination of mercury vapor in air have consisted in passing the air through a reacting liquid, followed by a colorimetric determination of the mercury. Gaglio² used a solution of palladous chloride, which was reduced, yielding free palladium in the form of black spots on the glass. Ménière³ passed the air through boiling nitric acid and determined the dissolved mercury colorimetrically by means of diphenylcarbazide. Blomquist⁴ treated the air in the room with chlorine to convert the mercury vapor to mercuric chloride and then passed the air through an absorption battery containing solutions of hydrochloric acid plus stannous chloride and potassium hydroxide. The mercury absorbed was determined by means of a rather complicated method, which in case of very small amounts of mercury would take several days to carry out. Turner⁵ washed the air in a spray of aqua regia in a Palmer dust machine and made use of the reverse of the Nessler test for the determination of mercury dissolved. He also tried amalgamation on gold leaf, measur-

A new indicator for mercury vapor of extremely high sensitivity has been found; indeed, there seems to be practically no lower limit to the concentration that can be detected. This method is based on the reaction between active selenium sulfide and the vapor. The selenium sulfide is applied as a coating to paper and the coated paper is blackened on exposure to the air containing mercury vapor, the degree of blackening being a function of time of exposure, concentration of the mercury and other factors, which can be definitely controlled. Apparatus has been developed by means of which it is possible to measure concentrations over a rather wide range.

ing the increase in weight, but this method gave lower results than the first.

All these methods are cumbersome and demand considerable time and skill. A method was therefore sought that would give quick results and not require chemical training to carry out. The principle on which such a method should be based was obviously a reaction between a solid substance and the

mercury vapor, with the reaction product a colored substance easily observable with the eye.

Development of Method

The best known reaction between mercury vapor and solids is that with such metals as gold, silver, or copper to form amalgams. No metal would give a sufficiently sensitive test, however, and it was necessary to seek another solid.

It was found that mercury vapor would react with freshly melted and cooled sulfur to form the black sulfide. This sulfur showed a fair sensitivity, which, however, disappeared entirely after a few days. It was evident from this that the reactivity was confined to one of the unstable forms of the element. This might be either the amorphous or the monoclinic form. With the hope of stabilizing one of these forms for trial it was proposed to join the sulfur with another substance which, if possible, would itself be reactive to mercury vapor. Selenium, the next element in the sixth periodic group, naturally suggested itself for this purpose.

Sulfur and selenium when melted together over a fairly wide range of proportions form sticky liquids, which on solidification give yellow, more or less plastic solids. On standing these gradually go over to a brittle state. This change is accelerated by heat.

The surface of these melts proved to be enormously more

¹ Presented in part before the Intersectional Meeting of the American Chemical Society, Niagara Falls, N. Y., January 29 to 30, 1926. Received August 13, 1926.

² Classen, "Analytischen Chemie," Vol. I, p. 46, Friedrich Vieweg und Sohn, Braunschweig, 1901.

³ *Compt. rend.*, **146**, 754 (1908).

⁴ *Ber. deut. pharm. Ges.*, **23**, 29 (1912); *Chem. Zentr.* 1126 (1913).

⁵ *U. S. Pub. Health Repts.*, **39**, 329 (1924); compare Jordan and Barrows, *THIS JOURNAL*, **16**, 898 (1924).

sensitive to mercury vapor than the pure sulfur surface. With a mixture containing 30 per cent selenium the reactivity was increased about twenty-five times. The reactivity, however, was still variable and lacking in permanency, though much better in the latter respect also than the sulfur.

Previous investigators⁶ of the constitution of these substances considered them, on the best evidence then obtain-

spottiness. The coatings were also found to turn red on exposure to light and heat with resultant decrease in their reactivity to mercury vapor.

All the difficulties encountered in the attempts to use a sol were overcome, and ultimately a means was furnished by which a film of standard reactivity could be produced, when it was discovered that the dry powder of selenium sulfide, if rubbed with a pad of cotton on paper having a smooth surface would adhere firmly, like graphite, forming a thin and uniform film.

First, however, it was necessary to develop a method by which a standard selenium sulfide—i. e., a product free from the plastic non-reactive form and from adsorbed selenious acid—could be made. As stated before, when hydrogen sulfide is introduced into a solution of selenious acid, the gas produces a yellow sol, which soon changes into a red plastic mass. It was found, however, that if the hydrogen sulfide is main-

tained in excess—i. e., if the selenious acid is added at a stoichiometric rate no faster than that at which the gas can be made to dissolve in the liquid—the yellow sol which is formed in the first instant will quickly flocculate, yielding a well-separated precipitate. Any excess selenious acid appears to act as a stabilizer for the colloidal sulfide, and when once formed the sol is entirely similar to that formed by passing the gas into the acid.

Since it proved difficult to maintain the rate of addition of acid necessary to produce the desired precipitate, a coagulant for the sulfide was sought. Aluminum chloride in small amount was found useful. Even with this, however, excess of selenious acid will still cause the formation of a sol, but unless in large amount this will coagulate as more hydrogen sulfide is absorbed.

The following procedure based on the foregoing observations is recommended:

Procedure for Making Active Selenium Sulfide

A solution of aluminum chloride containing about 100 mg. of aluminum per liter is saturated with hydrogen sulfide at room temperature, preferably in a flask that is partly closed in order

able,⁷ to be crystalline bodies of the monoclinic system. X-ray analysis⁷ showed, however, that they are in reality amorphous. Probably they must be regarded as solid solutions of a sulfur selenium, compound presumably selenium sulfide (SeS_2), in an excess of one or the other of the constituents.

On this view, the variability and lack of permanency in the reactivity seemed readily explainable on the supposition that the high reactivity might reside in the selenium sulfide, and that this was adversely affected by admixture with less active and stable forms of the component elements. The next step therefore was to obtain pure selenium sulfide in a form readily adaptable for use as a film or coating.

When hydrogen sulfide is passed into a solution of selenious acid, a yellow sol and a precipitate of a yellowish red color and a plastic consistency are formed together. Complete reaction does not seem to occur, since the solution formed always contains unchanged selenious acid, no matter how long the hydrogen sulfide is allowed to act. The precipitate is very voluminous and much of the acid solution is adsorbed. By pressing most of the liquid can be removed, but it does not seem possible to remove all the acid by washing. In this plastic form the precipitate has no reactivity to mercury vapor. On exposure to light or heat it soon turns red, presumably due chiefly to the free selenious acid present which is reduced. On drying a brownish red, brittle compound results, which can be ground to a fine powder.

When this powder was suspended in water or carbon disulfide, which partly dissolved it, and the suspension was painted on strips of paper, a yellowish red coat was obtained, the sensitivity of which was six- or sevenfold greater than any so far obtained—i. e., some two hundred times that of pure sulfur. But only the carbon disulfide suspension out of the several tried gave an adherent film, and this was not uniform, as small spots of relatively low reactivity appeared here and there, due to the variable composition of the products which crystallize out from a carbon bisulfide solution. Considerable time was spent in attempting to make a colloidal solution which would overcome these difficulties, and which could be used as a paint. However, it was not found possible, even with the aid of protective colloids, to prevent the red plastic modification of the sulfide from coagulating out. This formed a fine suspension which, when the mixture was applied to absorbent paper, filtered out upon the surface, rendering it inactive. On coated or glazed paper the filler or sizing tended to produce further coagulation, resulting in

⁶ Cf. Ringer, *Z. anorg. Chem.*, **32**, 183 (1902).

⁷ The writer is indebted to Dr. Wheeler P. Davey for these analyses.

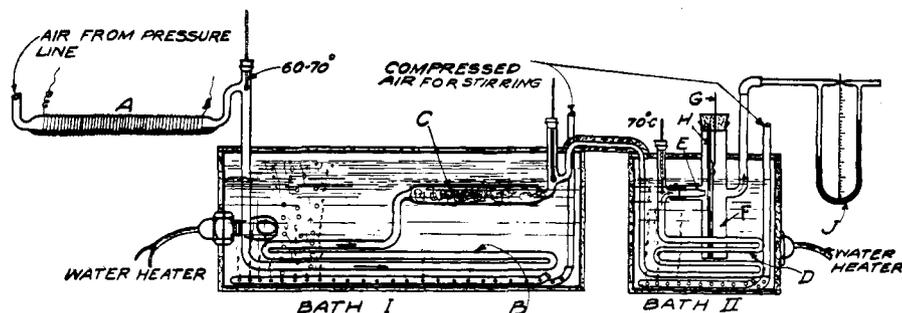


Figure 1—Apparatus for Studying Reaction between Active Selenium Sulfide and Mercury Vapor

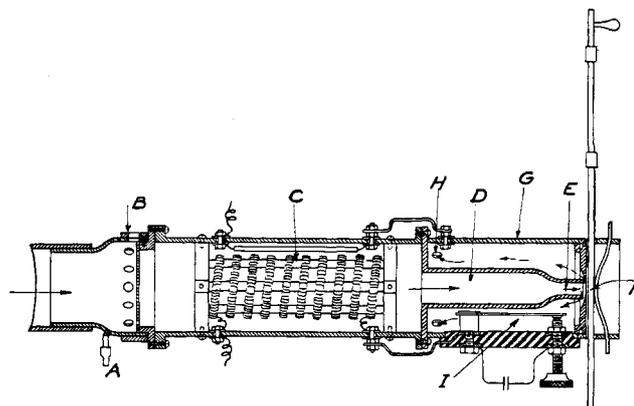


Figure 2—Diagram of Original Apparatus for Measuring Concentration of Mercury Vapor by Selenium Sulfide Method

to retain an atmosphere of the gas above the liquid and thus promote its absorption by the solution during the reaction. Vigorous mechanical stirring is also desirable for the same purpose. While continuing the current of hydrogen sulfide normal selenious acid solution is slowly added, delivering below the surface of the liquid in the flask. A yellow precipitate separates readily. A moderate temporary excess of the acid will form a sol which quickly clears up if the addition is stopped for the time,

but too much will give trouble. The operation should be carefully watched to keep the hydrogen sulfide in excess.

The precipitate is filtered, washed, and dried. It is a fine yellow powder, and can be dried on the steam bath without turning red. Short exposure to strong sunlight causes it to turn slightly reddish, but it goes back to yellow in darkness. Long exposure gives a permanent red to reddish violet. On rubbing, it becomes strongly electrified and it is probable that this electrification has some connection with the tenacity with which it adheres to paper. When kept in the dark no decrease in sensitivity to mercury vapor with age has been detected.

Application to Paper

The selenium sulfide is applied to the paper by dipping a pad of cotton wool into the powder and rubbing lightly over the surface until a uniform film, judging by the color, is formed.

The operation is easy if conditions are right. Among the most important of these conditions is the character of the paper. It should be smooth and dense, but not so highly glazed that adhesion and distribution of the powder are poor. The paper used in the writer's laboratory is "Warren's Cumberland Coated Paper, 70 lbs." A successful result is characterized by a surface of even light yellow and of a durability approaching that of a dyed surface. The powder can also be applied to other carriers, such as wood, finely ground or etched glass, celluloid, certain metals like lead, etc., to produce a surface sensitive to mercury vapor.

Reaction between Active Selenium Sulfide and Mercury Vapor

A study was undertaken of the reaction between the standard sensitized paper, obtained by the method described, and the mercury vapor. The relation between the reactivity and such factors as reaction temperature, velocity of the gas mixture against the paper, concentration of mercury in the air, and time of exposure have thereby been established. Some of the results, at least, should be applicable generally to solid-gas reactions.

PROCEDURE—Air from a pressure line is passed over mercury in a wide tube, *A* (Figure 1), heated so that the temperature of the outgoing gas is about 60–70° C. The gas saturated with mercury at this temperature is then passed through a coil system, *B*, of glass tubing immersed in a thermostat, *I*, to reduce the concentration of the vapor to that corresponding to the temperature of the thermostat, the excess of mercury being precipitated on the walls of the coil, forming a mirror. After passing through a cotton filter, *C*, to remove any mercury suspended in the air, the gas is led into the reaction system, which consists chiefly of a long coil, *D*, ending in a nozzle, *E*, in the reaction tube, *F*, all immersed in another bath, *II*, of a higher temperature than that of the thermostat. The gas, having attained the temperature of the bath, impinges normally upon the surface of the coated paper in the reaction tube. The coated paper is fastened on a movable slide, *G*, back of a diaphragm, *H*, with an opening registering with the orifice of the nozzle. A series of exposures can thus be taken at will. The velocity of the impinging gas current is measured and controlled by means of a flowmeter, *J*. To maintain the flow of gases through the apparatus either vacuum or air under pressure, taking the air from the room, is used. By changing the temperature of the first bath the concentration of mercury vapor in the air can be varied, and the reaction temperature can be varied by changing the temperature of the second bath. The concentration of mercury in the air at different temperatures has been calculated from Knudsen's data⁸ on the vapor pressure of mercury.

It was found that, other things being equal, the degree of blackening of the paper was directly proportional to the concentration of the mercury vapor and to the time of exposure. This means that, for the same degree of blackening, the time of exposure is inversely proportional to the concentration.

The effect of the linear velocity of the gas mixture on the reactivity was found to be proportional to the square root of the velocity. A velocity of one meter per second has been chosen as standard for the test. The effect of the temperature is more complicated, but tends to increase the

reactivity fairly rapidly. At this velocity the temperature coefficient (for 10 degrees increase in temperature) is about 1.2. For reasons connected with the testing of the flue gases from the mercury boiler, 70° C. has been chosen as the standard reaction temperature. The existence of a stagnant layer of air close to the paper, which must be penetrated by the vapor molecules before reaction with the surface can occur, is in evidence here. This is, of course, in keeping with the well-known film concept in heterogeneous reactions. The diffusion rate of the mercury vapor through this layer is the main factor which determines the rate of the reaction.

The reaction will not occur unless moisture is present. When the air was dried by passing over phosphorus pentoxide no reaction would take place, even at high temperature. On long exposure only a slight reddening of the paper would develop, indicating a breaking-up of the selenium sulfide.

At a velocity of one meter per second and at a reaction temperature of 70° C., a concentration of mercury in the air as low as 1 to 4 million by volume can easily be detected after 4 minutes' exposure. In fact, there seems to be no lower limit to the concentration which can be detected and measured in this way. It is merely a question of time of exposure. The reaction will take place readily at room temperature, although the time of exposure then has to be prolonged to produce a spot of the same density as at a higher temperature. Beakers containing mercury and covered with the SeS₂-coated paper have been placed out-of-doors during very cold days. The reaction occurred even at -15° C., at which temperature the concentration of the saturated air does not amount to more than 1 in 20 million and the diffusion rate of mercury is very low, although several hours of exposure were necessary before blackening appeared.

Color Scale for Estimation of Mercury Concentration

The relation of time of exposure to the degree of blackening furnishes a very simple way of making a color scale from which, by comparison with the results from a test with a gas of unknown mercury vapor content, almost any concentration can be estimated. A series of prints is made up at an arbitrarily chosen concentration, by varying the times of exposure. We can thus get the densities of the prints to increase in any convenient way, preferably in arithmetic progression. This series is naturally limited to the densities readily differentiated by the eye, but the range of concentrations can be indefinitely extended simply by changing the time of exposure. It is evident that by then applying the above relation the scale so produced can be calibrated and used to determine any concentration of mercury vapor. In case of low mercury concentration it is necessary to increase the time of exposure, but with high concentrations the reverse procedure should be adopted. In this way a scale has been made up which, by changing the time of exposure in geometric progression from 8 minutes to 1 minute, can be used to measure any concentration between 1:8,000,000 to around 1:15,000, the latter corresponding to the saturation of air with mercury at the standard reaction temperature, 70° C. Higher concentrations can be measured by increasing the

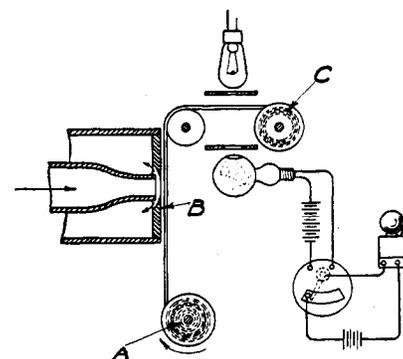


Figure 3—Device for Continuous and Automatic Registration

Higher concentrations can be measured by increasing the

⁸ *Ann. Physik*, **29**, 179 (1909).

reaction temperature so as to raise the saturation value of the air, and by decreasing the time of exposure. The method, however, is primarily designed for the detection of very small concentrations of mercury in air, and other methods might be preferable at high concentrations.

Portable Apparatus

A portable apparatus has been developed in which the standard conditions can be maintained, so that it is now possible to measure the concentration of mercury vapor in

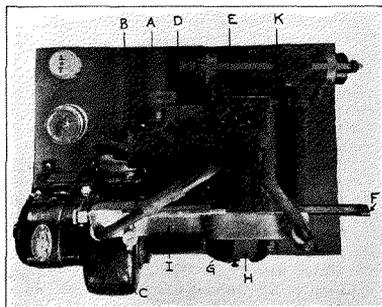


Figure 4—Top View

A—Inlet tube
B—Outlet tube
C—Blower
D—Heater

Recent Apparatus of Intermittent Type
E—Thermoregulator
F—Thermometer
G—Housing

any desired locality. The main features are best shown by Figure 2, which is a section of the first apparatus built. The air, or gas, to be analyzed for mercury is blown into the apparatus by means of a small blower (not shown), the velocity of the air current being measured by a pressure gage at A, which serves as a flowmeter. By turning the ring, B, the incoming air current may be bled off, making possible an adjustment of the velocity. The air then passes over the electric heater, C, and thence into the tube, D, which ends with the nozzle, E. The arrangement, F, for exposing the sensitive paper to the vapor is similar to that shown in Figure 1. After striking the paper, the air is turned back into the annular space between the nozzle and the housing, G, and is discharged through the holes, H. In this space it passes over the adjustable thermoregulator, I, which controls the heating current. This apparatus is designed for intermittent use.

For continuous and automatic registration the system shown in Figure 3 is used. A continuous strip of the coated paper is slowly drawn over the opening in the diaphragm, B, by means of a small clock motor attached to C. A short time after exposure the color produced can be viewed from above and compared with a standard scale mounted beside the paper. A permanent record for a whole day can be obtained with this apparatus. By using a photo-electric cell circuit, as indicated, it has been demonstrated feasible to express the degree of blackening—i. e., the concentration of mercury—in terms of milliamperes. Arrangement can then be made so that a signal is given when the concentration exceeds a certain limit.

Figures 4 and 5 show a more recent apparatus of the intermittent type designed for general use constructed on the same principle, but improved in mechanical details. Instead of pressure, suction is used, which has proved to be of

practical advantage. The velocity is adjusted by controlling the speed of the motor driving the blower. To attain better heat insulation and to make it possible to use the apparatus for corrosive gases, like flue gases, Bakelite is used throughout.

Effect of Other Vapors

So far, the selenium sulfide seems to be sensitive only to mercury vapor. From a chemical standpoint it seems probable that the vapors of all the heavy metals having black sulfides will give an indication. Rubbing the selenium sulfide

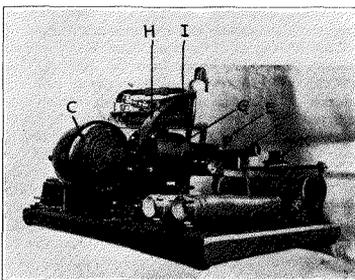


Figure 5—Side View

H—SeS₂ paper (exposed side turned out to show prints made on exposure)
I—Flowmeter
K—Motor rheostat

on copper and silver will immediately cause the corresponding sulfides and selenides to form. The vapor pressures of these metals at ordinary temperatures are so low, however, that it would take a very long time before any visible blackening would occur, unless in actual contact. This makes the reaction virtually specific for mercury. Mercury ions in solution do not seem to have any reactivity with the indicator; the mercury must be either in the liquid or vapor state to react.

Acknowledgment

The writer wishes to express his indebtedness to Charles Van Brunt, under whose supervision this research has been conducted, for his kind interest and guidance, and for the many valuable suggestions he has given during its progress. The development of new improved apparatus is due to the efforts of T. H. Swisher.

Isopropyl Alcohol in the United Kingdom

There is a steadily increasing use of isopropyl alcohol in the United Kingdom, chiefly as a substitute for ethyl alcohol in the manufacture of the cheaper grades of perfumes and flavoring essences. Isopropyl alcohol is produced in Great Britain by the catalytic reduction of acetone. This process has given it a reputation for freedom from offensive after-odor on evaporation, and in this respect is claimed to be superior to the method of production prevailing in the United States. The British product contains 95 to 96 per cent of isopropyl alcohol, the remainder being water.

The prohibitive duty on ethyl alcohol had practically done away with the sale of cheap spirituous perfumes, but isopropyl alcohol has helped greatly in the partial revival of the production and trade in popular perfumes at prices within the purchasing power of the middle classes. For this purpose isopropyl alcohol is preferably blended with ethyl alcohol, thus reducing the cost of the solvent and also helping to avoid the odor of isopropyl alcohol which is stated to be heavy and persistent when used alone.