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NAVAL RESEARCH LABORATORY
WASHINGTON 20, D. C.THE DEVELOPMENT OF A CHEMICAL
AGENTS DETECTOR KIT

by

JOHN A. KRYNETSKY

Chemistry Division-Prot. Chemistry Section
Report No. P-2540; Problem No. P-60

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Approved by

W. C. Lanning,

Head, Protective Chemistry Section

P. Borgstrom, Superintendent.
Chemistry DivisionA. H. Van Keuren, Rear Admiral, USN
Director, Naval Research Laboratory

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Abstract

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ABSTRACT

A chemical warfare agents detector kit was developed which contains tests for the detection of the vapors of AC, CK, CG, L, H, HN and gross surface contamination by H or L. The tests included were selected on the basis of their sensitivity, stability, specificity and ease of performance. The kit is compact, easily carried and sufficiently rugged to withstand the abuses encountered when worn by men undergoing amphibious and other combat training. In general, the kit was found to have a good tropical storage stability.

Apparatus and methods were developed for the construction and manufacture of the kit and a limited number were successfully produced, at a reasonable cost, by a commercial firm.

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INTRODUCTION

Authorization

1. This work was authorized under Bureau of Ships Project Order No. 397/44. Problems proposed for study were given in Bureau of Ships letter S-S77-2(Da) Serial 811 dated 17 December 1940. Development of a C.W. agent detector kit was requested in Bureau of Ships letter S77-2-(5)(688) of 18 March 1944.

Statement of the Problem

2. The objects of this work were:

(a) To develop a chemical warfare agents detector kit of the gas absorption type which would be simple to operate and suitable for use by the Naval forces.

(b) To develop apparatus and methods for use in the construction and manufacture of such kits.

Known Facts Bearing on the Problem

3. The C.W.S. and the O.S.R.D. have done a great amount of work on the detection of war gases and the publications of these agencies describe a number of various types of gas detection systems.

4. The C.W.S. has developed a gas detector kit known as the "Chemical Agents Detector Kit, M9". This kit contains glass tubes that are filled with silica gel impregnated with certain gas-detecting chemicals. It contains five different types of gas detector tubes and three types of liquid reagents which are necessary in performing some of the tests. It will detect the following war gases: H, HN, ED, MD, L, CG and CK.

5. The advantages of the M9 kit are:

(a) It is compact and easy to operate.

(b) The tests for H, HN, ED, MD and CG are sensitive and reasonably specific.

(c) The detector tubes are protected from contamination by means of lead tube jackets and are stable for long periods of storage.

(d) The kit is of rugged construction and capable of withstanding rough handling.

(e) The kit has proven to be adaptable to manufacture on a large scale.

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6. The disadvantages of the kit are:
- (a) The confirmatory test for HN and the tests for L and CK are poor.
 - (b) The kit has no provisions for the detection of AC.
 - (c) The lead tube jackets which are used to protect the detector tubes are difficult to remove by inexperienced personnel.
 - (d) Several of the tests are indirect and require special treatment for their development.

Theoretical Considerations

7. In the limited time available for the development of a Navy Gas Detector Kit, it was deemed highly improbable that a simple kit could be developed which would detect all of the known chemical warfare agents. Work was restricted therefore, toward the detection of only those agents which it was felt were most likely to be employed by the enemy. In this connection, it was thought unnecessary to include detectors for the lachrymatory and harassing agents such as CN, BBC, DM, DA, ED, MD, etc., as these agents make themselves self-evident in very low concentrations which are not likely to produce injury. On the other hand, it was thought desirable to include detectors for the vapors of the blister gases (H, HN, L), the choking gas (CG) and the nerve and blood poisons (AC, CK). It was also felt advisable to provide for the detection of gross surface contamination by the blister gases.

8. In the development of the Navy Gas Detector Kit, it was judged that the kit should satisfy as many as possible of the following standards:

- (a) The kit should contain tests for the detection and identification of the vapors of AC, CK, CG, L, H and HN. It should also contain tests for the detection of gross surface contamination by H, HN and L.
- (b) The tests should have sufficient sensitivity to detect the agents in concentrations below damaging.
- (c) The tests should be rapid and reasonably specific.
- (d) The operation of the kit should be kept as simple as possible so that inexperienced personnel can use it with a minimum of instruction.
- (e) The kit should be compact and suitable for use both aboard ship and in the field.

- (f) The kit and all components should have adequate stability toward storage over long periods of time.
- (g) The kit should be of sufficiently rugged construction to withstand rough handling.
- (h) The kit should be adaptable to mass production at a reasonable cost.

Previous Work Done at This Laboratory

9. Previous work related to this problem has been presented in N.R.L. Report No. P-2223, "A Critical Evaluation of the Performance of the Army M-9 Chemical Warfare Agents Vapor Detector Kit", dated 28 January, 1944 and in N.R.L. letter C-S77-2 (459-BBB), Ser. C-459-18/45, "Manufacture of the Navy Gas Detector Kit, Mk-1", dated 26 January, 1945, to Chief of the Bureau of Ships (688).

EXPERIMENTAL

Part I - Adaptation and Development of Gas Detectors

A. The AC Detector

10. In the search for a suitable method for detecting AC, the following type reactions were thought worthy of consideration:

- (a) Reaction of AC with alkaline sodium picrate (yellow) to form isopurpuric acid (red-brown).
- (b) Reaction of AC with cupric sulfide (black) to form cuprous cyanide (white).
- (c) Reaction of AC with iron salts to give ferric ferrocyanide (Prussian blue).
- (d) Reaction of AC with a cupric salt to give a cuprous salt which in turn reacts with a reagent for cuprous ion to produce a color change.
- (e) Reaction of AC with mercuric chloride to form hydrogen chloride which produces a color change with an acid-base indicator such as metanil yellow.
- (f) Reaction of AC with a cupric salt-organic amine reagent to produce a color change.

(1) Reaction of AC with Alkaline Sodium Picrate

11. Several formulations of gels (both silica and alumina base) containing sodium picrate and sodium carbonate were prepared: These gels had good sensitivity to AC but were not considered satisfactory because the color change (yellow to brownish-red) was slow to develop and was not sharp enough for easy identification.

(2) Reaction of AC with Cupric Sulfide

12. A silica base gel containing cupric sulfide was prepared. Its sensitivity and color contrasts were too poor for it to be considered as a possible AC detector.

(3) Reaction of AC with Iron Salts

13. Several possible methods for the formation of the Prussian blue color were considered. Preliminary examination of these methods indicated that this type of test would be complicated and unduly long to perform.

(4) Formation of Color Due to Cuprous Ion

14. AC reacts with cupric salts to form cyanogen and cuprous cyanide. Several attempts were made to prepare detectors based on the reaction of the cuprous salt with agents such as dimethylaminobenzalrhodanine to produce a color change. These experiments were unsuccessful and no further work was done along this line.

(5) Reaction of AC with Mercuric Chloride-Metanil Yellow

15. Several formulations of silica base gels containing mercuric chloride plus the acid-base indicator, metanil yellow, were prepared. The most successful of these was one containing 0.5% mercuric chloride + 0.1% metanil yellow. This gel was found to have a high sensitivity to AC. The color change upon exposure to AC was from yellow to red-purple.

16. From the beginning, it was obvious that any acidic agent present in the sampled atmosphere would also give a positive test and that the tube would be of doubtful value. In order to increase its utility, a section of silica gel impregnated to hold 0.10% metanil yellow (gel A) was placed in the tube ahead of the AC-detecting gel (gel B). In this tube, an acid agent should give a positive test in both gels A and B whereas AC should give a negative test in gel A and a positive test in gel B. A number of these two-section tubes were exposed to various agents to check their behavior. The results of these tests are given in Table 10.

17. From Table 10, it is seen that practically all acidic agents such as CG, L, ED, crude H, FS, HCl, HI, etc., give positive tests on both gels A and B. In addition, gun fumes and the agents CK, SA, H₂S

and SO₂ behave in an analogous manner to AC by giving a negative test in gel A and a positive test in gel B. The agents Cl₂, PS, nitric fumes, and chlorinated H interfere by giving colors other than red-purple with both gels A and B.

18. Because of the many agents which interfere with the detection of AC by means of the mercuric chloride-metanil yellow test, it was desirable to search for a more satisfactory AC detector.

(6) Reaction of AC with a Cupric Salt - Organic Amine Reagent

19. The formation of color by the reaction of AC with a cupric salt-organic amine type reagent, is a well known sensitive method of detecting AC. Such reagents have been investigated both at this Laboratory and at the CWS Development Laboratory at M.I.T. and have been discussed with them in conference. The advantages of this method are that it is rapid, direct and fairly specific in nature. The principal disadvantage of this method is the lack of stability of the various formulations proposed previously. However, this reaction offered the most promise and efforts were directed toward:

(a) A search for a cupric salt - organic amine combination which is sensitive to AC and which is adaptable to the tube type detector.

(b) A search for a means of stabilizing the gel in the detector tube.

20. A number of organic amines were impregnated onto silica gel containing cupric sulfate. These were then tested qualitatively for reactivity to AC. The results of these tests are given in Table 1. Of these compounds, compound No. 12, tetramethyldiaminodiphenylmethane (TDM) was chosen for further study on the basis of superior sensitivity, stability and color contrast (pale blue to dark blue).

21. The spoilage of tubes containing a cupric salt - organic amine type detector gel appeared to be due to slow oxidation by the atmospheric oxygen in the sealed tube. In order to verify this, a number of tubes containing cupric sulfate-TDM-salicylic acid gel were prepared and sealed in a nitrogen atmosphere. After 21 days storage at 60°C, these tubes showed no signs of spoilage, whereas tubes prepared and sealed in air were stable for only 5 days at 60°C.

22. Two methods of stabilizing the tube were tried: (a) the inclusion of an antioxidant in the gel and (b) the incorporation of a "getter" in the tube to remove the oxygen.

23. Use of Antioxidants - A number of gels were prepared by impregnating silica gel with 1.5% CuSO₄·5H₂O, 0.1% TDM and 0.5% antioxidant. These gels were tested for relative sensitivity and color change. Sealed tubes containing these gels were tested for storage

stability at 60°C. The results of these tests are given in Table 2.

24. Of the compounds tested, salicylic acid offered the most promise as a stabilizing agent since the gel retained a good sensitivity and color change. This was not true for the other agents tried.

25. Use of oxygen "getters" - Several oxygen "getters" were considered of which two were selected as being representative. They were magnesium metal and charcoal.

26. A number of glass detector tubes were prepared in which the filling consisted of a 1 cm. section of cupric sulfate-TDM-salicylic acid gel. A few pieces of magnesium turnings were placed in the ends of tubes, and the tubes were sealed. The magnesium was "fired" by heating so as to remove the oxygen. It was found that the magnesium became so hot that it reacted with the glass and caused a considerable weakening of the tube. No further work was done along this line.

27. Previous work at this and other laboratories has shown that activated charcoal is an effective agent for the removal of atmospheric oxygen from a closed system. Accordingly, impregnated PCI charcoal and plain coconut charcoal were tried as "getters". Preliminary experiments showed that the "whetlerized" charcoal liberated enough ammonia to turn the detector gel bluish and was thus unsatisfactory. The coconut charcoal seemed to have no detrimental effects on the detector gel.

28. A number of sealed glass detector tubes were prepared in which the filling consisted of a 1 cm. section of cupric sulfate-TDM-salicylic acid gel, and a 0.5 to 1.5 cm. section of charcoal. The two sections were separated by means of a small disc of organdy. The charcoal used was prepared by equilibrating 12-30 mesh coconut charcoal with air at 40°C and 80% R.H. This was then ground and sieved to a 40-60 mesh size. The stability of tubes prepared in this manner is given in Table 3.

29. From Table 3 it is evident that a section of protecting charcoal as small as 0.5 cm. is sufficient to give the tube good stability.

30. The sensitivities of the charcoal-containing tubes, given in Table 4 are expressed as the concentration of AC which may be readily detected on drawing a 200 ml. sample of gas mixture through the tube.

31. It can be seen from Tables 3 and 4 that the use of 0.5 cm. of protective charcoal in the tube is sufficient to stabilize the tube without materially affecting the sensitivity of the gel after storage.

32. Effects of Other Agents on Test - Cupric sulfate-TDM-salicylic acid tubes were exposed to a number of different agents to determine if any other agents besides AC would give a positive test and if the exposure to other agents would interfere with the production of color on

exposure to AC. The results of these tests are listed in Table 11.

33. It can be seen from Table 11 that the only agents tried besides AC which will give a positive test with the TDM tube are low concentrations of chlorine and high concentrations of ammonia or ethylenediamine. The colors produced by high concentrations of ammonia and ethylenediamine are due to the formation of cuprammonium type complexes. The low concentrations likely to be encountered in the field would not be expected to interfere with the test.

34. FM, low concentrations of HCl and relatively high concentrations of ED and nitric fumes decrease the sensitivity of the TDM tube to AC. FS, H₂S and high concentrations of HCl and chlorine destroy the sensitivity of the tube to AC. The acidic agents probably interfere by reacting with the TDM to form a salt. The oxidizing agents probably interfere by the destruction of the TDM. H₂S interferes due to the formation of copper sulfide.

35. As stated in paragraph 20, the color change of the cupric sulfate-TDM-salicylic acid gel upon exposure to AC, is from a pale to a darker blue. Although this color change is quite definite to an experienced observer, it was felt that the inexperienced person might have trouble in recognizing this change when trying to detect low concentrations of AC. Accordingly, it was thought that the original color of the gel might be neutralized by the inclusion of a small amount of some inert reddish dye. Several such dyes were tried and it was found that the incorporation of 0.00010% of the DuPont dye TLA #35 (diazotized anthranilic acid coupled with diethyl aniline) resulted in a gel which appeared nearly white when placed in a detector tube. Upon exposure to AC, the gel turned blue. The sensitivity of tubes containing this gel was not altered and the test color was such as to be recognized more readily by inexperienced personnel. Upon storing such tubes at 60°C for 30 days, the gel turned to a very pale green-blue color but still retained its sensitivity. Tubes stored at room temperature for 6 months have shown no signs of deterioration.

B. The CK Detector

36. In the search for a suitable method for detecting CK, the following systems were considered:

- (a) Reaction of CK with thio-Michlers' ketone to produce a blue color.
- (b) Reaction of CK with DB3 to form a yellow color.
- (c) Reaction of CK with a DB3 gel sensitized with an organic primary amine to produce a pink-red color.

(1) Reaction of CK with thio-Michler's Ketone

37. Further investigation of this method for detecting CK

revealed that thio-Michler's ketone is very unstable when impregnated onto various types of gas-absorption media. Therefore work on this reagent was dropped.

(2) Reaction of CK with DB3.

38. The reaction of CK with pyridine type compounds is a well known method for detecting CK. In this reaction, DB3 is one of the more sensitive pyridines. When silica gel is impregnated to hold 1% DB3, the original color is white and the gel has excellent stability. Upon sampling CK, a direct yellow to orange color is produced. This color becomes more intense on standing and reaches a maximum intensity after approximately 2 minutes. Using a 200 ml. sample, the test was found to detect CK when present in a concentration of 50%/l.

(3) Reaction of CK with DB3-Aniline

39. Organic primary aromatic amines may be used as sensitizers in the reaction between CK and pyridine type compounds. The presence of such an amine increases both the sensitivity of the reaction and the intensity of the test color. Silica gel was impregnated to hold 1% DB3, and then aniline was added by means of a vapor-phase impregnation. The original color of such a gel is white to very pale yellow. Upon sampling CK, a direct pink to red color is produced. As in the case of the unsensitized DB3 gel, the test color becomes more intense upon standing and does not reach its maximum intensity until approximately 2 minutes after sampling. Using a 200 ml. sample, this gel was found to detect CK readily when present in a concentration of 25%/l. (See Table 5). Sealed glass detector tubes containing this gel were found to be stable for 30 days at 60°C. (See Table 5). A number of detector tubes containing this gel were exposed to various agents to determine the effect of these agents upon the gel. The results of these tests are given in Table 12.

40. An inspection of Table 12 shows that none of the agents tried, with the exception of CK and CB, give positive tests. Relatively high concentrations of FS, FM, SO₂ and nitric fumes and low concentrations of chlorine reduce the sensitivity of the tube toward CK. High concentrations of chlorine and HCl destroy the activity of this detector gel.

C. The CG Detector

41. The reaction of CG with p-dimethylaminobenzaldehyde and aromatic amines is a well known sensitive method for the detection of CG. The CG test found in the Army M-9 kit makes use of this reaction. The gel contained in the M-9 tubes is composed of washed silica gel impregnated to hold 5% p-dimethylaminobenzaldehyde and 5% phenyl-x-naphthylamine with 0.10% of thiourea added as a stabilizer. The color of this gel is yellow and is turned directly green upon exposure to CG.

Using a 200 ml. sample, this gel was found to detect CG readily when present in a concentration of 25 v/l. (See Table 5). This sensitivity was found to be virtually independent of humidity. Sealed glass detector tubes containing this gel were found to be stable for >30 days at 60°C. (See Table 5). A number of detector tubes containing this gel were exposed to various agents to see the effects of these agents on the gel. The results of these tests are given in Table 13.

42. From Table 13 it is seen that high concentrations of chlorine render this detector insensitive toward CG and that FS and high concentrations of nitric fumes interfere with the test. The agents PS, Crude L, low concentrations of nitric fumes, HCl, ethylenediamine and fumes from burning fuel oil and CC-2 impregnated clothing reduce the sensitivity of the test toward CG.

D. The L Detector.

43. In the search for a suitable L detector, the following methods were considered:

(a) The reaction of L with sodium chloraurate in an alkaline medium to produce a grey color.

(b) The reaction of L with a molybdate to produce a blue color.

(c) The reaction of L with cuprous salts in an alkaline medium to produce a red-brown color.

(1) Reaction of L with Sodium Chloraurate.

44. When silica gel impregnated with sodium chloraurate is exposed to L and a few drops of 10% caustic are added, a reduction of the sodium chloraurate takes place accompanied by a change in color of the gel from yellow to grey-black. Several variations of this gel were prepared. These were, however, considered unsatisfactory as they were found to have poor storage and light stabilities when placed in sealed glass detector tubes.

(2) Reaction of L with Molybdates.

45. The Army M-9 kit contains a general arsenicals detector which is composed of silica gel impregnated with 5.5% each of ammonium molybdate and zinc sulfate. This gel is pale greenish-yellow in color and is turned blue on exposure to an agent such as ED, MD, or L. When placed in sealed glass detector tubes, this gel was found to have a stability of >30 days at 60°C. The sensitivities of this gel toward ED and L are given in Table 8.

46. An inspection of Table 8 shows that under dry conditions

this detector has a good sensitivity toward ED and a fair sensitivity toward L. However, it is evident that with an increase in humidity, the sensitivity falls off rapidly so that when the relative humidity becomes 50% or greater, this gel is almost worthless for detecting L. This failure to detect L under conditions of moderate and high humidities is largely overcome in the M-9 kit by adding a few drops of 10% caustic to the exposed tube.

(3) Reaction of L with Cuprous Salts in an Alkaline Medium.

47. The detection of L by means of cuprous salts in an alkaline medium is based on the fact that L is decomposed by alkali to yield acetylene which reacts with cuprous salts to produce red-brown cuprous acetylide. Inasmuch as L is the only common war gas which liberates acetylene when treated with alkali, this method of detection is specific for L and gives no test with the other arsenical agents.

48. Silica gel was impregnated with cuprous iodide by passing a solution of potassium iodide through silica gel which had previously been impregnated with cupric sulfate. The original color of this gel is white to light grey-blue. Upon sampling L through a tube containing this gel and subsequently adding a few drops of 10% caustic, a red-brown ring is formed near the intake end of the tube. Sealed glass detector tubes containing this gel were found to be stable for >30 days. (See Table 6.) The sensitivities of this gel are given in Table 6.

49. It may be seen from Table 6 that this gel has a fair sensitivity toward L and that this sensitivity is practically constant and independent of the concentration of agent present. It is also seen that, unlike the zinc molybdate gel, this gel is but slightly affected by conditions of high humidity.

50. A number of detector tubes containing this gel were exposed to various agents to determine the effects of these substances on the gel. The results of these tests are given in Table 14.

51. From Table 14, it is seen that this test is specific for L and that the only agents which render it insensitive are CK and high concentrations of nitric fumes. The agents PS, high concentrations of chlorine, low concentrations of nitric fumes, H₂S and fumes from burning fuel oil reduce the sensitivity of the test toward L. Oil smoke interferes by giving a slight yellow-brown color with the tube.

E. The Mustards Detector.

52. In the search for a suitable mustards detector, the following methods were considered:

(a) The reaction of H or HN with sodium chloraurate in an alkaline medium to produce a grey color.

(b) The reaction of H or HN with thio-Michler's ketone

to give a blue color.

(c) The reaction of HN with an acid-base indicator to give a color change.

(d) The reaction of HN with a Dragendorff reagent to give a color change.

(e) The reaction of H or HN with DB3 to produce a blue color.

(1) Reaction of H or HN with Sodium Chloraurate or Thio-Michler's Ketone.

53. The limitations of both of these reagents as chemical detectors have already been discussed in paragraphs 44 and 37.

(2) Reaction of HN with Acid-Base Indicators.

54. The HN's are of themselves basic in nature and will, accordingly, turn the acid color of certain indicators into the base color. The Army M-9 kit contains a detector tube which is based on this reaction and is used to differentiate the HN's from H. This tube contains silica gel impregnated with the acid form of the indicator phloxine. The original color of the gel is white to pale pink. When HN is sampled through this tube, a pink band is formed near the intake end. The sensitivity of this tube was found to be 3-7 r of HN under dry conditions and as low as 20 r HN-3 at high humidities (see Table 9a). Inasmuch as the original test for the mustards is approximately 20 times as sensitive as this one (see paragraph #57), this tube was not considered to be very satisfactory.

(3) Reaction of HN with A Modified Dragendorff Reagent.

55. The HN's have the property of forming colored addition products with certain inorganic salts. The Army M-9 kit contains a confirmatory test for the HN's, which is based on this property. This test is used in conjunction with the phloxine tube test for the HN's (See paragraph #54). A liquid reagent which is composed of bismuth oxychloride, sulfamic acid, potassium iodide and distilled water* is added to the exposed phloxine tube. A positive test is evidenced by the formation of an orange band at the intake end of the gel and is accompanied by a general yellow color, due to the reagent itself, throughout the entire length of the tube filling.

56. The sensitivity of this reagent, under dry conditions,

*This solution is a modification of one proposed by Dragendorff as a general test for alkaloids and is therefore spoken of as the "Dragendorff" Reagent.

was found to be approximately the same as for the phloxine tube (3-5 v HN). Under humid conditions, a slightly reduced sensitivity of 5-8 v HN was found (see Table 9b). Because of the low sensitivity for HN of this reagent as compared with the excellent sensitivity of the original mustards test (see paragraph 58), the Dragendorff test was not considered to be very satisfactory.

(4) Reaction of H or HN with DB3.

57. DB3 reacts with many alkylating agents to produce quaternary ammonium salts which are converted by means of caustic to the quaternary ammonium hydroxides. The latter spontaneously split out water to form the dehydro compounds which are in many cases colored substances. Since the mustard gases are alkylating agents, they give this reaction. In the case of the mustard gases, the color produced is blue. The Army M-9 kit contains a tube for the primary detection of H and HN which is based on this reaction. The gel fill of this tube consists of silica gel impregnated to hold 1% of DB3 and 0.5% of sodium bicarbonate (the latter is added to stabilize the gel). The initial color of this detector is white and the developed mustards test appears as a blue band at the intake end of the gel. On silica gel, the initial reaction between H or HN and DB3 is slow at ordinary temperatures (requires 15 or more minutes). However, if the reaction is heated to 80°C or more, it is greatly accelerated and takes place in 30 seconds or less. The mustards detector tubes found in the M-9 kit are provided with chemical heating pads to accelerate the test (see paragraph 73).

58. Sealed glass detector tubes containing this gel were found to be stable for a period of 30 days (See Table 7). The sensitivities of this gel toward H and HN under various conditions are given in Table 7.

59. It is seen from Table 7, that the sensitivity of this detector toward H and HN is excellent under all conditions of toxic agent concentration and relative humidity tested.

60. A number of these detector tubes were exposed to various agents to determine the effects of these substances on the gel. The results of these tests are given in Table 15.

61. From Table 15, it is seen that high concentrations of chlorine and HCl destroy the activity of this detector. The acidic agents CG, ED, L, PS; low concentrations of HCl and nitric fumes; HC, FM and oil smoke; and fumes from burning fuel oil reduce the sensitivity of the test toward H. The agents CK, CN, and PS, interfere by giving colors with this detector. Due to the non-persistent nature of most of the above agents, it is believed that concentrations likely to be encountered in the field would not constitute serious or prolonged interference.

F. The Detection of Gross Surface Contamination by Blister Gases.

62. Although the silica gel absorption type tubes described in

paragraphs 43 through 61 can be used for the detection of gross surfaced contamination by the blister gases, it was considered that this method would be too laborious and would require an undue expenditure of tubes. In an effort to find a suitable detector for surface contamination, several detectors were tested.

(1) C.W.S. M-6 Liquid Detector Paper.

63. This paper is coated with an O.D. color paint which contains an oil-soluble dye. This detector gives a brilliant red color with liquid blister gases and many other solvents. The test is made by placing the coated side against the contaminated surface.

(2) Differential Detector Powder.

64. This powder is similar to the British "differential" detector powder described in Porton Report No. 2489. It was prepared at this Laboratory and has the following formula:

<u>Ingredients</u>	<u>Parts by Weight</u>
Silica gel (200-300 mesh)	10
Pot shell grog (60-200 mesh)	90
Dye (TLA-28)	0.1
Dye (TLA-29)	0.01
Dye (TLA-30)	0.1

To make a test the powder is sprinkled lightly over the suspected surface. The presence of a liquid blister gas will cause the original color (pink) to be turned to one of the following colors: orange-red with H, purple-red with L, and yellow-orange with HN-3.

(3) C.W.S. M-7 Crayon.

65. This crayon contains Congo Red indicator, CC#2 and inert materials. It is used by making a crayon mark on the suspected surface. The color change is red to blue for a positive test. As alternatives, the crayon may be used to mark paper which is placed face down against the contaminated surface or it may be pulverized by hand and sprinkled over the surface.

(4) Comparison Tests for Gross Contamination Detectors.

66. In testing these detectors, four representative types of surfaces were used; steel painted with Navy deck paint; unpainted wood, concrete, and earth. Pure blister gases (H, L, HN-3) were put on these surfaces in drops and the surfaces were tested immediately to observe the reaction of the detectors with the liquid. In addition, tests were made on similarly contaminated surfaces at various time intervals after the liquid vesicant had been absorbed. With the wood and painted steel panels, the tests were conducted at 35°C. With these surfaces using H as the contaminant, comparative tests were made with Congo Red S-328 test

paper which is used for laboratory decontamination tests. All of the other tests were made at room temperature (Ca. 25°C). The results of these tests are given in Tables 16, 17, 18 and 19.

67. From Tables 16-19 it is seen that the M-6 paper is practically insensitive to vapors of the blister gases and will give a test only when the actual liquid is present. The "differential" detector powder detects the presence of liquid blister gases and very high vapor concentrations of HN-3. It is, however, practically insensitive to vapors of H or L. The M-7 crayon is sensitive to liquid and high vapor concentrations of H and L. The crayon, is, however, insensitive to HN-3. Of the various forms of the M-7 crayon, the crayon mark and marked paper are more sensitive than the powdered crayon.

G. Conclusions to Part I.

68. From the foregoing work, it was concluded that the most satisfactory detectors for inclusion into a field detector kit are the following:

<u>Agent</u>	<u>Type Detector</u>	<u>Paragraph Reference</u>
AC	Copper salt - organic amine gel	19
CK	DB-3 Aniline gel	39
CG	p-dimethylaminobenzaldehyde-phenyl -α- naphthylamine gel	41
L	Cuprous iodide gel	47
H, HN	DB3 gel	57
Surface Contamination	C.W.S. M-7 crayon	65

69. Details for the preparations of the above detector gels are given in Appendix C.

PART II - Other Problems Related to the Development of the Detector Kit.

A. Problems Related to the Preparation of Detector Tubes.

(1) Packaging Gels in Detector Tubes.

70. It was decided to package the detector gels into sealed pyrex glass tubes (4 mm. O.D. x 3" long) provided with 2 light scratch marks located 3/4" from each end (to facilitate opening) as shown in Plate 1. In the cases of the CK, CG, L and H-HN detectors, the fill consists of a 9 mm. section of the appropriate gel supported between gel-retaining plugs and is located in the central portion of the tube. In the case of the AC detector, the central fill consists of a 5 mm. section of AC detector gel and a 5 mm. section of protective charcoal separated by a gel-spacing plug and supported by gel-retaining plugs. As gel-retaining and spacing plugs a double thickness of white American Organdy, Heberline Process permanent finish, 76x72 thread count cut to 3/8 by 3/8 inch squares or 3/8 inch diameter discs was found to be entirely satisfactory.

71. In order to secure the fill and prevent it from being sucked out upon taking a sample of gas, the use of a small wire plug-retaining spring was adopted to anchor one of the gel-retaining plugs in place. In the AC detector, it is the plug retaining the charcoal that is fixed; in the other detectors, either plug may be fixed. In using these tubes, it is this end bearing the plug-retaining spring that is inserted in the suction pump.

72. As a means of identification, it was decided to provide each tube with a small dot of colored lacquer near the end bearing the plug-retainer spring and just below the scratch mark. The following colors were chosen to identify the tubes:

<u>Detector</u>	<u>Identifying Color</u>
AC	Brown
CK	Orange
CG	Green
L	Yellow
H, HN	Blue

(2) Heater for the Mustards Detector Tube.

73. As stated in paragraph 57, the reaction between H or HN with DB3 which is slow at ordinary temperatures is greatly accelerated if heated to 80°C or more. In the Army M-9 kit, this heating is accomplished by means of a chemical heating pad attached to the tube. This pad is composed of a 5/8 inch square of unfluffed "Webril 1062" treated with a wetting agent and wrapped around the approximate center of the tube. A 1/2 inch square of 0.002 inch aluminum foil is wrapped around the Webril and the whole is cemented together by means of a nitrocellulose cement. In order to work this heater, a 30% solution of cupric chloride

is applied by means of an eye dropper until the foil is discolored and steam appears. The disadvantages of this heater are:

- (a) It is difficult to construct properly.
- (b) Inasmuch as the wetting pad is placed beneath the aluminum foil, it is difficult to apply the cupric chloride solution properly without undue wastage of this reagent.
- (c) The heating action is not positive and experiments have given erratic results.

74. In an effort to overcome the disadvantages of the above heater, the following heating methods were considered:

- (a) Heating by use of a match or cigarette type lighter
- (b) Heating by means of a friction type heater and
- (c) Heating by means of a modified M-9 type chemical heater.

75. Heating by Use of a Match or Cigarette Type Lighter.

Although this is often a simple, convenient and satisfactory method for heating the DB3 tube, there are times when its use would be either very difficult or undesirable. There is also the danger of overheating when using this method.

76. Heating by Means of a Friction Heater.

Several friction heaters were devised. The most successful of these is shown in Plate 3. In using this heater, the tube to be heated is placed in the small brass tube located at the head of the device. The cord is then drawn taut and the heater is moved back and forth in much the same manner as used when stropping a razor. With this arrangement, temperatures of 90°C or greater are readily obtained in 50 strokes or less. It was found that either cotton shoe-lace or nylon string could be used as the friction cord and that the heater would function satisfactorily either wet or dry.

77. Despite the many advantages of this heater, it was not considered to be entirely satisfactory for the following reasons:

- (a) It is rather bulky and could easily become lost.
- (b) The friction cord has a definite life so that replacements are necessary, and
- (c) The heat produced is a variable depending on the tension of the cord, length of stroke and rapidity of stroke.

78. Heating by Means of a Modified M-9 Type Chemical Heater.

Several modifications of the M-9 heater were devised.

It was found that more positive heating action could be obtained by a reversal of the aluminum foil and wetting pad (i.e. placing the foil next to the glass tube and wrapping the wetting pad around the foil). In making this reversal, it was found that a more durable material than Webril must be used as the wetting pad. Upon testing a number of different materials as wetting pads, it was found that bleached muslin treated with a wetting agent was satisfactory from the standpoints of mechanical strength, wet strength, heat produced, wettability and glueability.

79. Tests have shown that heaters prepared in the above fashion consistently produce temperatures of 90°C or greater. Inasmuch as the wetting pad is wrapped around the aluminum foil, it is easier to apply the cupric chloride solution so that wastage of this reagent is kept at a minimum. Practice has shown this heater to be easier to construct than the original M-9 heater. Heaters of this type have been found to be stable for periods of 30 days at 60°C.

(3) Sealing Detector Tubes.

80. The use of sealed pyrex glass tubes to package detector gels (see paragraph 70) necessitated the development of a rapid method for sealing 4 mm x 3" pyrex glass tubes. To accomplish this, several automatic sealing machines were designed and built. The most successful of these is shown in Plate 4. This machine is equipped with a self-feeding hopper which holds approximately 300 tubes. It has two sealing stations so that both ends of the tube are sealed during one pass through the sealer. Sealing is accomplished by means of the oxygen-gas burners located at each sealing station. During each sealing period (approximately 4.8 seconds), the tube is constantly rotated by means of supporting rollers, so that a uniform seal is produced. Under continuous operation, one such machine is capable of producing 1296 seals equivalent to 648 detector tubes per hour. Experience has indicated that this machine is capable of producing glass-sealed tubes on a mass production scale.

(4) Filling Gels into Detector Tubes.

81. As stated in paragraph 70, the CK, CG, L and H-HN detectors are each filled with a 9 mm. section of the appropriate gel and the AC detector is filled with a 5 mm. section of AC detector gel and a 5 mm. section of protective charcoal. In order that tubes could be filled, uniformly, on a mass production scale, and in the manner prescribed above, it was necessary that a filling device be designed and constructed. The device built to accomplish this operation is shown in Plate 5. It is designed on the principle of a granular soap dispenser. The gel is placed in the hopper located at the top of the device and is metered by means of the drilled slide-plate to 10 tubes at one stroke and is delivered into the tubes by gravity. The amount of gel delivered on one stroke is governed by the thickness of the slide-plate and by the diameter of the holes drilled in the slide-plate. The filling device is constructed so as to accommodate two different slide plates; one meters out 9 mm. sections of gel into tubes and the other 5 mm. sections of either gel or charcoal.

82. During the filling operation, the tubes are held by means of drilled wooden or bakelite blocks as shown in Plates 5 & 6, (fig. 1.). The holes in these blocks are drilled to coincide with the gel-delivery holes of the filler. In addition, there is located at the base of each hole, a 1/4" thick disc of sponge rubber to allow vertical movement of the tubes. This movement allows each tube to fit snugly against its gel-delivery hole in the filler, in order to avoid spillage of the gel. Experience has indicated that the above described devices and methods are entirely suited for use in mass production.

(5) Scoring Detector Tubes.

83. As stated in paragraph 70, it is necessary to provide each sealed glass detector tube with light scratch marks located near each end to facilitate opening of the tube. In order to accomplish this, a semi-automatic detector tube scoring device, shown in Plate 7 was developed and constructed with the cooperation of the Norwich Pharmacal Company of Norwich, New York. In this device, a tube is picked up from a feed-hopper by means of a slotted drum holding 2 diamond pointed pencils. As the drum is rotated, the tube is passed directly under 2 rubber-tipped fingers which cause the tube to be rotated against the diamond points for one complete revolution. After the scoring is completed, further rotation of the drum causes the tube to be dropped into a collection bin. The diamond points and rubber-tipped fingers are located so that the scratch marks are placed 1-1/2" apart and approximately 3/4" from each end of the tube. The diamond pointed pencils are mounted so that the pressure of the points against the tube may be adjusted. This adjustment of pressure allows the production of score marks of any desired depth.

84. It has been found that this device is capable of producing uniform scratch marks, free from any spiral, around the entire periphery of the tube. Experience has indicated that this device is suited for use in mass production and that one operator can turn out 3600 scored tubes per hour.

(6) Insertion of Gel-Retaining Plugs.

85. The organdy plugs used to retain the detector gels in the tubes (paragraph 70) may be inserted with the aid of the plug-plunger and plug-setting jig (developed with the cooperation of the Norwich Pharmacal Company of Norwich, N. Y.), shown in Plate 8. The folded organdy plugs, held in the tray of the jig, are centered over the Beveled holes and are driven into the tubes, to a predetermined depth, by means of the plug-plunger.

86. In order to put the plugging operation on a semi-automatic basis, it was deemed advisable to develop a plug-cutting and setting machine. Such a machine is shown in Plates 9 & 10. The organdy is fed, in double thickness, from a roll through the instrument. Motion of the elevated hand-lever causes a gang punch to cut the organdy into 10 double thickness $3/8$ " diameter discs and then causes a gang plunger to insert these discs, to a predetermined depth, into the tubes. During this operation, the tubes are held by means of the same drilled blocks used in the filling operation (see paragraph 82). The gang plunger is readily removable and replaceable by plungers of different lengths so that plurs may be set to any desired depth. Laboratory experience has shown this machine to produce rapidly plugs which are far superior in tightness, neatness and uniformity to those produced by the hand method. Thus far, enough experience has not been had with this machine to conclude whether or not it is suited for use in mass production.

B. Packaging of Detector Tubes and Crayons.

87. The use of sealed glass detector tubes necessitated that methods of packaging be found that would protect the tubes and minimize their breakage. Of the methods tried, the most satisfactory are shown in Plate 2. In the cases of the CK, CG and L detectors, it was decided to package the tubes in groups of 17 into cellulose acetate vials ($1 \times 3-1/8$ ") "honeycombed" with seventeen $2-1/2 \times 3/16$ " cellophane straws and closed by cork-lined metallic screw-caps. As additional protection, it was decided to line the inner walls of the vials with 0.040" felt paper and the bottoms with $3/16$ " cotton batting. In the case of the AC detector, the packaging method adopted is the same as above except that a larger vial ($1-1/4 \times 3-1/8$ ") is used to hold 27 tubes. In the case of the H, HN detector, it was found that the cloth-heating-pad (paragraph #78) provided sufficient protection to eliminate the necessity of using the cellophane straws. It was therefore decided to package these tubes in groups of 25 into $1-1/4 \times 3-1/8$ " vials as above but without the cellophane straws.

88. In order to facilitate identification, it was decided that the vials and screw caps used to package the tubes should be colored in agreement with the scheme used in paragraph 72.

89. In the case of the vesicant detector crayons, M-7, it was decided to cut them to 3" lengths and package them in groups of 3 into black cellulose acetate vials ($1 \times 3-1/8$ ") containing $3/16$ " layers of cotton batting at the bottoms and closed by means of cork-lined black metallic screw-caps. (See Plate 6, Fig. 2).

C. Other Components of Kit.

(1) Pump for Kit.

90. In choosing a suitable air-sampling pump for use with

the Navy kit, it was decided to adopt the pump developed by the C.W.S. for use in the Army M-9 kit (see Plate 11).

(2) Packaging of Liquid Reagents.

91. In packaging the sodium hydroxide and cupric chloride liquid reagents which are necessary to perform some of the tests (paragraphs 48, 57, and 79), it was decided to adopt 1/2 oz. French square bottles equipped with plastic screw-caps bearing glass dropping pipettes and neoprene-rubber compounded dropping bulbs. It was decided to furnish each kit with one blue-painted bottle of 10% sodium hydroxide solution and one aluminum-painted bottle of 30% cupric chloride solution.

(3) Solid Reserve Chemical Reagents.

92. It was decided to provide each kit with one cork-stoppered, blue-painted 1/2 dram shell vial filled with 1.5 grams of sodium hydroxide pellets and with two cork-stoppered, aluminum-painted, 1 dram lip vials filled with 5.5 grams of anhydrous cupric chloride for use as emergency replenishments of the liquid reagents (paragraph 91). As a method of packaging, it was decided to place these within the hollow space of the air-sampling pump handle (paragraph #90). For added protection, it was decided to seal each vial in a cellophane jacket and to place pads of cotton batting in the hollow cylinder of the pump both below and above the reagent-filled vials.

(4) General Instructions for Use of Kit.

93. As a means of instruction, a 10 page booklet was prepared. This booklet is composed of 5 sheets of white, opaque vinylite (7-1/4" x 2-5/8") printed on both faces, laminated on each face with clear vinylite and is bound together by small metal rings. The complete text of these instructions and the calculation of safe exposure times to vapors of H, HN and L are given in Appendix D. The text of these instructions contains the following:

Page 1 - General instructions including the gases detectable by the kit, value of the kit, and methods of sampling.

Pages 2 - 6 - Instructions for performing the various tests and color comparison charts to indicate the relative concentration of the gas detected. Each page is devoted to the use of one tube; the instructions for its use are given on the left side and the color comparison charts on the right.

Pages 7 - 8 - Tables of safe exposure times to vapors of H, HN and L for men both protected and unprotected by masks.

Page 9 - Instructions for use of the M-7 vesicant detector crayon.

Page 10 - General remarks covering the replenishment of exhausted liquid reagents, emergency performance of tests in case the droppers for the liquid reagents should break and the examination of tubes in

the dark.

(5) Carrier for Kit; Vial Block.

94. Several carriers (both box and canvas-case type) for holding all of the components of the kit were designed and constructed. The final carrier adopted (shown in Plate 13) is of the canvas case type and was developed with the cooperation of the District Awning and Shade Co. of Washington, D. C. It is composed of double thickness No. 8, shade O.D. #7, water and mildew-proofed cotton duck. It measures 8-3/4" x 5-3/4" x 3-1/4" and is provided with a 50" adjustable web-canvas shoulder strap. The case contains three compartments as follows: one cylindrical pump-carrying pocket 1-7/8" x 8", one 3" x 7-1/2" front flat pocket for holding the direction cards and one 2-3/4" x 3-3/4" x 7-1/2" main body pocket for holding the vial-block (paragraph 95). The case is stiffened in front and back by including 0.030" "Fish-board" between the layers of canvas. The two closure flaps are held fast by means of mud-proof "Lift the Dot" snap fasteners.

95. The vial block (See Plate 12) is made of hard wood protected with two coats of a mildew-proof, water resistant varnish and measures 2-11/16 x 2-3/8 x 7-1/2". It contains nine compartments for holding six vials of detector tubes, one vial of detector crayons and two bottles of liquid reagents. It is fastened into the carrier by means of three 5/8" round head brass escutcheon pins.

D. Manufacture of the Kit.

96. A set of specifications was drawn up at this Laboratory and 1700 detector kits were manufactured by the Norwich Pharmal Company of Norwich, New York. for the Bureau of Yards and Docks under Contract No. N-130-S-9715P at a unit cost of \$20.20. Complete details concerning the manufacture of these kits are given in the Naval Research Laboratory letter, C-S77-2(459-BBB), Ser. C-459-12/45, Manufacture of the Navy Gas Detector Kit, MK-1, dated 26 January, 1945, to Chief of the Bureau of Ships (688). The complete kit and component parts are shown in Plates 14 & 15.

Part III - Storage and Service Trials of Kits.

A. Breakage of Tubes Resulting from Dropping of Kit.

97. Several complete kits were dropped, in various positions, from a height of 4 feet onto different surfaces so as to determine the degree of breakage that might result from rough handling. Drops were also made in which the kits contained vials only half full of tubes to determine the effect of "packing" on breakage. After each drop, the kits were examined and the broken tubes were counted and replaced by new ones. The results of these tests are given in Table 20. The figures given are averages expressing the percentage of tubes broken per drop. From Table 20, it is seen that the most severe breakage occurred when the kit landed flat on its back on some hard surface such as concrete. When the kit landed in other positions or on softer surfaces the breakage was reduced sharply.

B. Tropical Storage of Kit.

98. One kit was placed in a tropical storage chamber operating on an alternating, 24 hour, heat-humidity cycle. The conditions existing in this chamber, for one complete cycle, are: 12 hours at 45°C (113°F) and 80% R.H. followed by 12 hours at room temperature and 90% R.H. The kit was periodically examined for deterioration of its various components. The results are given in Table 21.

99. From Table 21, it is seen that in general the kit has adequate tropical storage stability (6 months). The components having the poorest stability are the flashlight battery (6 weeks) and the CG detector (4-5 months). Some of the metal parts were heavily corroded at 6 months, but were still usable. The crayons showed mechanical deterioration at 6 months but could still be used to test for surface contamination. The AC detector showed no deterioration at 2 months, the total time it had been in storage.

C. Wearing Trials of Kit.

100. Six kits, complete except for direction cards, were issued to N.C.O.'s attached to a Marine unit undergoing amphibious training at Camp Lejeune, North Carolina during the period of August 16-18, 1944. In addition, most of these kits were reissued for an additional five day period to men undergoing combat training on rifle ranges during the period of August 21-25. The kits were carried, slung from the shoulder, throughout the entire operations.

(1) Activities during Wearing of Kits.

101. The men spent most of the first day practicing on the transport mock-up, climbing up and down landing nets. Late in the afternoon, the first landing operation took place. The boats formed waves and ran full speed up to the beach. The men charged the beach over barbed wire and through blank machine gun fire and demolition charges planted in the sand. A high sea was running and all of the men were thoroughly soaked with salt water, and also by a steady rain which accompanied the landing. In addition, some of the men were forced to

embark from the boats in water ranging from knee to neck deep as the boats were stopped short of the actual beach. During the charges across the beach and afterwards, when the men rested, the kits were well exposed to sand.

102. Most of the second day was spent on practice in extended order drill through woods and on practice on landing nets. Later, a second landing was made, similar to the first, except that there was no rain.

103. On the third day, the landings were transferred to the shore of the inland waterway, and the men went through three landing maneuvers. The men did not get wet, but the kits were exposed all day to the hot sun and sand.

104. The first day of training on the rifle range was spent on general instructions in the care and use of the rifle. The rest of the week was spent in firing on ranges simulating combat conditions. During this time, the kits were thoroughly exposed to sand, dirt, mud, hot sun, several hours of hard rain, many shocks and barbed wire and other snags.

(2) Examination of Kits.

105. At the end of these operations, the kits were collected and later returned to this Laboratory for examination. They were received approximately six weeks after the conclusion of the wearing trials. The results of these trials are given in Table 22. From Table 22, it is seen that no serious damage was caused to the kits and that they were in good operating condition after the wearing trials.

SUMMARY AND CONCLUSIONS.

106. A number of reagents for the detection of the vapors of C.W. agents have been studied. Of these reagents, the following were chosen as best suited for use in a gas detector kit:

- (a) Copper salt - organic amine gel for AC
- (b) DB3 - aniline gel for CK
- (c) p-dimethylaminobenzaldehyde-phenyl - α -naphthylamine gel for CG
- (d) Cuprous iodide gel for L and
- (e) DB3 gel for H-HN.

These gels were packaged into sealed glass tubes provided with scratches near the ends to facilitate opening. Tests are performed by drawing the suspected air through the tubes by means of a pump. The tests for AC, CK, and CG are direct, whereas the tests for the vapors of L and H-HN are indirect, requiring further manipulation for their completion. The C.W.S. M-7 crayon was chosen as best suited for the detection of

gross surface contamination by H and L.

107. The above detectors have been incorporated into a compact kit, contained in an olive-drab cotton duck carrying case (8-3/4" x 5-3/4" x 3-1/4") provided with a 50 inch adjustable web-canvas shoulder strap. The complete kit weights approximately 2.9 pounds.

108. Apparatus and methods have been developed for the construction of sealed glass tubes and manufacture of the kit. A limited number (1700) of kits were successfully produced, at a reasonable cost, by a commercial firm.

109. The kit was sufficiently rugged to withstand the abuses encountered when carried by men during three days of amphibious operations and five days of additional combat training. However, some damage to the contents of the kit was sustained when the kit was subjected to rather severe dropping tests. In general, the kit was found to have good tropical storage stability except for the flashlight battery (in the pump handle) which deteriorated within six weeks.

RECOMMENDATIONS.

110. None. The results of this work has been made available to the Bureau previously and a limited number of kits have been manufactured.

APPENDIX A

TABLES 1 - 22.

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TABLE 1

Test of Reactivity of Cupric Salt -
Organic Amine Gels to AC.

<u>Organic Amine Used</u>	<u>Test</u>	<u>Color Change</u>
1. Aniline	+	
2. o-phenylenediamine	+	
3. p-Toluidine	+	
4. p-Phenetidine	+	Good
5. Diphenylamine	+	Good
6. Dimethylaniline	+	
7. N-benzylaniline	+	Poor
8. Phenyl -o-naphthyl amine	+	Poor
9. Bis(p-methylaminophenyl) methane	+	Fair
10. Michler's ketone	+	Poor
11. Dibenzylaniline	+	Poor
12. Tetramethyldiaminodiphenyl- methane (TDM)	+	Good
13. N-(p-phenetyl) morpholine	+	Fair-good
14. N-(p-anisyl) morpholine	+	Fair-good
15. Anthranilic acid	-	
16. Acetoacetanilide	-	
17. Diacetyl p-phenylenediamine	-	
18. Pyridine	+	
19. Quinoline	+	
20. Piperidine	-	
21. Morpholine	-	
22. Butylamine	-	
23. Dibutylamine	-	
24. Tributylamine	-	
25. Diacetyl ethylenediamine	-	
26. Dibenzylamine	-	

TABLE 2

Performance of TDM-Copper Sulfate
Gels Containing Antioxidants

<u>Stabilizing Agent</u>	<u>Relative Sensitivity</u>	<u>Color Change</u>	<u>Stability* at 60°C (days)</u>
None	Good	Good	1
Salicylic Acid	Good	Good	5
Tyrosine	Good	Good	1
Cysteine hydrochloride	Fair	Good	5, 30**
Sodium hypophosphite	Fair	Good	1
Benzaldehyde	Fair	Fair	Not tested
Thiosalicylic acid	Fair	Fair	" "
Stannous chloride	Fair	Fair	" "
Oxalic acid	Insensitive	-	" "
Thiourea	Insensitive	-	" "

*Stability was taken as the number of days at which the first signs of deterioration became noticeable.

**This gel became speckled at the end of 5 days, but did not deteriorate further for a period of greater than 30 days, at which time it was still serviceable.

TABLE 3

Stability of TDM-Copper Sulfate
Tubes Containing Charcoal

<u>Length of Charcoal Section</u>	<u>Stability at 60°C (days)</u>
0.0 cms.	5
0.5 "	> 38
1.0 "	> 38
1.5 "	> 38

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TAB^{LE} 4

Sensitivities* of 1% Copper Sulfate
Tubes containing charcoal

A. Fresh Tubes (no charcoal)

<u>R. H.</u>	<u>Sensitivity</u>
Ca. 0%	50 r/l.
Ca. 50%	50 r/l.
Ca. 100%	50 r/l.

B. Tubes Aged for 38 Days at 60°C

<u>Length of Charcoal Filling</u>	<u>Sensitivity at Ca. 50% R.H.</u>
0.5 cms.	50 r/l.
1.0 "	100 r/l.
1.5 "	100 r/l.

*Sensitivities expressed as concentration
of toxic agent (expressed in micrograms per liter)
required to produce a positive readable test upon
drawing a 200 ml. sample through the detector tube.

TABLE 5

SENSITIVITIES & STABILITIES OF AC, CK & CG DETECTORS

<u>Detector</u>	<u>Sensitivity* at R.H. of</u>			<u>Sensitivity* at Ca. 50% R.H. after 30 Days Storage at 60°C</u>
	<u>Ca-0%</u>	<u>Ca-50%</u>	<u>> 90%</u>	
AC	50	50	50	50
CK	25	10	10	25
CG	25	25	25	25

*Sensitivities expressed as concentration of toxic agent (expressed in micrograms per liter) required to produce a positive readable test upon drawing a 200 ml. sample through the detector tube.

TABLE 6

SENSITIVITIES AND STABILITY OF THE L DETECTOR (Cu_2I_2)

<u>Condition of Tube</u>	<u>R.H.</u>	<u>Toxic Conc.*</u>	<u>Sensitivity**</u>
Fresh	0%	5	5
"	0%	10	5
"	0%	50	5
"	50%	10	7
"	80%	10	6
Stored 30 days at 60°C	0%	10	5

* Concentrations are expressed in micrograms (μ) toxic agent per liter.

** Sensitivities are expressed in μ toxic agent required to produce a positive test.

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TABLE 7
SENSITIVITIES AND STABILITY OF THE H, HN DETECTOR (DB-3)

Condition of Tube	R.H.	Toxic Conc.*	Sensitivity** toward		
			H	HN-3	HN-1
Fresh	0%	5	0.25	0.15	0.05
"	0%	10	0.25	0.10	
"	0%	50	0.25	0.15	
"	50%	5	0.50	0.15	
"	80%	5	0.25	0.15	
Stored 30 days at 60°C	0%	5	0.5-1		

* Concentrations are expressed in micrograms (5) toxic agent per liter.

** Sensitivities are expressed in toxic agent required to produce a positive test.

TABLE 8
SENSITIVITIES* OF THE GENERAL ARSENICALS DETECTOR TUBE (molybdate)
TOWARD ED & L

Agent	0% R.H. & Toxic Conc.**			Conc. = 5 / l. & R.H. of	
	5	10	50	50%	80%
ED	2	1	1	15	40-50
L	7	9	10	> 50	> 50

* Sensitivities are expressed in micrograms (5) toxic agent required to produce a positive test.

** Concentrations are expressed in toxic agent per liter.

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TABLE 9a

SENSITIVITIES* OF THE HN DETECTOR (PHLOXINE TUBE)

Agent	<u>0% R.H. & Toxic Conc**</u>			<u>Conc = 5 g/l & R.H. of</u>	
	<u>5</u>	<u>10</u>	<u>50</u>	<u>50%</u>	<u>80%</u>
HN-3	5	5	7	6	20
HN-1	3		7	5	7

TABLE 9b

SENSITIVITIES* OF THE HN DETECTOR (DRAGENDORFF REAGENT)

Agent	<u>0% R.H. & Toxic Conc**</u>			<u>Conc = 5 g/l & R.H. of</u>	
	<u>5</u>	<u>10</u>	<u>50</u>	<u>50%</u>	<u>80%</u>
HN-3	5	5	3	6	8
HN-1	5		5	5	7

* Sensitivities are expressed in micrograms (g) toxic agent required to produce a positive test.

** Concentrations are expressed in g toxic agent per liter.

TABLE 10

INTERFERENCE TESTS ON MERCURIC CHLORIDE-METANIL YELLOW TUBE

<u>Agent</u>	<u>Test on Gel A</u>	<u>Test on Gel B</u>
AC	-	+
CK	-	+
CG	+	+
Cl ₂	blue	blue
SA	-	+
CN	-	-
CNS	+	+
CNB	-	-
BBC	-	-
PS	Brown-purple	Brown-purple
ED	+	+
L(pure)	+	+
L(crude)	+	+
H(pure)	-	-
H(crude)	+	+
HL	+	+
Chlorinated H	brown	brown
HN-1	-	-
HN-3	-	-
PF-3	-	-
DA	-	-
FS	+	+
HC	+	+
WP	+	-
NO, NO ₂	Red-brown	Red-brown
TCE	-	-
NH ₃	-	-
HCl (high conc.)	+	+
HCl (low conc.)	+	+
Tobacco smoke	-	-
Ethylenediamine	-	-
Car exhaust fumes	-	-
Burning fuel oil	-	-
Burning CC-2 (impreg.cloth)	+	+
H ₂ S	-	+
SO ₂	-	-
Gun Fumes		
(a) 5" rifle		
(1) At shell casing	-	+
(2) Discharge cloud	-	+
(b) 40 mm. machine gun		
(1) Breech cloud	-	+
(2) Discharge Cloud	-	+

TABLE 11

Tests for Interfering Agents
on TDM-copper Sulfate Tubes.

<u>Agent</u>	<u>Test</u>	<u>Effect on AC Test</u>
AC	+ (blue)	-
CK	-	None
CG	-	"
Cl ₂ (low conc.)	Sl. +	Exposure to AC deepens color
Cl ₂ (high conc.)	-	Exposed tube insensitive
SA	-	None
CN	-	"
CNS	-	"
CNB	-	"
BBC	-	"
PS	-	"
ED	-	Exposure decreased sensitivity
L (pure)	-	None
L (crude)	-	"
H (pure)	-	"
H (crude)	-	"
HL	-	"
Chlorinated H	-	"
HN-1	-	"
HN-3	-	"
PF-3	-	"
DA	-	"
DC	-	"
FS	-	Exposed tube insensitive
HC	-	None
FM	-	Exposure decreases sensitivity
WP	-	None
Oil Smoke	Sl. yel.	"
NO, NO ₂	"	Exposure decreases sensitivity
TCE	-	None
NH ₃ (high conc.)	Sl. +	Exposure to AC deepens color
NH ₃ (low conc.)	-	None
HCl (high conc.)	Sl. yel.	Exposed tube insensitive
HCl (low conc.)	-	Exposure decreased sensitivity
Tobacco Smoke	-	None
Ethylenediamine	Sl. +	Exposure to AC deepens color
Car exhaust fumes	-	None
Burning fuel oil	Sl. black	Color due to smoke filtered in tube
Burning CC-2	Sl. black	" " " " " " " "
(impreg. cloth)		
H ₂ S	Brown	Exposed tube insensitive
SO ₂	-	None

TABLE 12

TESTS FOR INTERFERING AGENTS ON CK DETECTOR
(BB3 - ANILINE)

<u>Agent</u>	<u>Test</u>	<u>Effect on CK Test</u>
CK	+	-
CB	+	-
AC	-	None
CG	-	"
Cl ₂ (low conc.)	sl. blue	Exposure decreases sensitivity
Cl ₂ (high conc.)	yellow	Exposed tube insensitive
SA	-	None
CN	-	"
CNS	-	"
CNB	-	"
BBC	-	"
PS	-	"
ED	-	"
L (pure)	-	"
L (crude)	-	"
H (pure)	-	"
H (crude)	-	"
HN-1	-	"
HN-3	-	"
PF-3	-	"
DA	-	"
FS	-	Exposure decreases sensitivity
WP	-	None
HC	-	"
Oil smoke	sl. tan-orange	"
FM	-	Exposure decreases sensitivity
NO, NO ₂	sl. yel.-green	Exposure decreases sensitivity
TCE	-	None
NH ₃	-	Imparts a purple color to CK test.
HCl (low conc.)	-	None
HCl (high conc.)	-	Exposed tube insensitive
Tobacco smoke	-	None
Ethylenediamine	-	"
Car exhaust fumes	-	"
Burning fuel oil	Black ring due to filtering of smoke	Sensitivity slightly reduced.
Burning CC-2 (impreg. cloth)	-	None
H ₂ S	-	"
SO ₂	-	Exposure decreases sensitivity
Gun fumes		
(a) 5" rifle		
(1) At shell casing	-	Not run
(2) Discharge cloud	-	" "
(b) 40 mm. machine gun		
(1) Breech cloud	-	" "
(2) Discharge cloud	-	" "

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TABLE 13

TESTS FOR INTERFERING AGENTS ON CG DETECTOR
(p-dimethylaminobenzaldehyde-phenyl- α -naphthylamine)

<u>Agent</u>	<u>Test</u>	<u>Effect on CG Test</u>
CG	+	-
DP	+	-
CK	sl. orange	None
AC	-	"
Cl ₂ (low)	-	"
Cl ₂ (high)	greenish-brown	Exposed tube insensitive
SA	-	None
CN	-	"
CNS	-	"
CNB	-	"
BBC	-	"
PS	dirty green	Exposure decreases sensitivity
ED	sl. orange	" " "
L (pure)	-	None
L (crude)	sl. orange	Exposure decreases sensitivity
H (pure)	-	None
H (crude)	-	"
HN-1	-	"
HN-3	-	"
PF-3	-	"
DA	-	"
FS	green	Interferes
HC	-	None
FM	-	"
WP	-	"
Oil smoke	sl. orange	"
NO, NO ₂ (low)	sl. orange	Exposure decreases sensitivity
NO, NO ₂ (high)	green	Interferes
TCE	-	None
NH ₃	-	"
HCl (low)	sl. orange	Exposure decreases sensitivity
HCl (high)	orange-yellow	Sensitivity greatly reduced.
Tobacco smoke	-	None
Ethylenediamine	-	Exposure decreases sensitivity.
Car Exhaust Fumes	-	None
Burning fuel oil	black ring due to filtering of smoke	Sensitivity slightly reduced.
Burning CC-2 (impreg. cloth)	sl. orange	Exposure decreases sensitivity.
H ₂ S	-	None
SO ₂	-	"
Gun fumes		
(a) 5" rifle		
(1) At shell casing -		not run
(2) Discharge cloud -		" "
(b) 40 mm. machine gun		
(1) Breech cloud -		" "
(2) Discharge cloud -		" "

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TABLE 14

TESTS FOR INTERFERING AGENTS ON L DETECTOR
(Cu₂I₂)

Agent	Test	Effect on L Test
L (pure)	+	-
L (crude)	+	-
HL	+	-
AC	-	None
CK	-	Exposed tube insensitive
CG	-	None
Cl ₂ (low)	-	"
Cl ₂ (high)	-	Exposure decreases sensitivity.
SA ₂	-	None
CN	-	"
CNS	-	"
CNB	-	"
BBC	-	"
PS	-	Exposure decreases sensitivity.
ED	-	None
H (pure)	-	"
H (crude)	-	"
HN-1	-	"
HN-3	-	"
PF-3	-	"
DA	-	"
FS	-	"
FM	-	"
HC	-	"
WP	-	"
Oil smoke	sl. yel.-brown	Interferes slightly
NO, NO ₂ (low)	-	Exposure decreases sensitivity.
NO, NO ₂ (high)	-	Exposed tube insensitive.
TCE	-	None
NH ₃	sl. blue	"
HCl (low)	-	"
HCl (high)	-	"
Tobacco smoke	-	"
Ethylenediamine	-	"
Car exhaust fumes	-	"
Burning fuel oil	Black ring due to filtering of smoke	Exposure reduces sensitivity
Burning CC-2 (impreg. cloth)	-	None
H ₂ S	sl. yellow-brown	Exposure decreases sensitivity.
SO ₂	-	None
Gun fumes		
(a) 5" rifle		
(1) At shell casing -		Not run
(2) Discharge cloud -		" "
(b) 40 mm. machine gun		
(1) Breech cloud -		" "
(2) Discharge cloud -		" "

TABLE 15

TESTS FOR INTERFERING AGENTS ON H, HN DETECTOR
(DB3)

<u>Agent</u>	<u>Test</u>	<u>Effect on H Test</u>
E (pure)	+	-
H (crude)	+	-
HN-1	+	-
HN-3	+	-
HL	+	-
AC	-	None
CK	yellow-red	Interferes
CG	-	Exposure decreases sensitivity.
Cl ₂ (low)	-	None
Cl ₂ (high)	-	Exposed tube insensitive.
SA	-	None
CN	sl. +	Interferes slightly
CNS	sl. rose ring	None
CNB	-	"
BBC	sl. rose ring	"
PS	rose to red purple	Interferes
ED	-	Exposure decreases sensitivity
L (pure)	-	" " "
L (crude)	-	" " "
PF-3	-	None
DA	-	"
FS	-	Exposure decreases sensitivity
FM	-	" " "
HC	-	" " "
Oil smoke	sl. brown	Interferes slightly
WP	-	None
NO, NO ₂ (low)	-	"
NO, NO ₂ (high)	-	Exposure decreases sensitivity
TCE	-	None
NH ₃	-	"
HCl (low)	-	Exposure decreases sensitivity
HCl (high)	-	Exposed tube insensitive
Tobacco smoke	-	None
Ethylene diamine	-	"
Car exhaust fumes	-	"
Burning fuel oil	Black ring due to filtering of smoke	Exposure decreases sensitivity
Burning CC-2 (impreg. cloth)	-	None
H ₂ S	-	"
SO ₂	-	"
Gun fumes		
(a) 5" rifle		
(1) At shell casing-		Not run
(2) Discharge cloud-		" "
(b) 40 mm. machine gun		
(1) Breech cloud sl. brown		" "
(2) Discharge cloud -		" "

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TABLE 16

COMPARISON OF DETECTORS FOR GROSS SURFACE CONTAMINATION

Surface - Steel painted with Navy deck paint.

Time - (minutes) after contamination at which test is still obtainable.¹

Test Method	Contaminant		
	2,5,6	3,5	4,5
	H	L	HN-3
M-6 Paper	60 - 90	90	8-16 hrs.
"Differential" detector powder	60 - 90	1 - 30	>24 hrs.
M-7 crayon mark	90 - 120	>480	No test
M-7 crayon paper	120	>480	" "
M-7 crayon powder	60 - 90	90	" "

1. A test was called negative if no appreciable color changes occurred within 5 minutes.
2. Liquid H still visible at 60 minutes; at 90 minutes, no liquid visible.
3. Liquid L blistered paint and was rapidly absorbed; no liquid visible at 5-10 minutes.
4. Liquid HN-3 still visible at 8 hrs.; at 16 hrs., no liquid visible.
5. Temperature of tests using H, 35°C; using L and HN-3, 25°C.
6. C.R. Paper S-328 test times: at 90 mins. - 0.3 to 0.4 mins.; at 120 mins - 0.5 to 0.6 mins.

TABLE 17

COMPARISON OF DETECTORS FOR GROSS SURFACE CONTAMINATION

Surface - Wood (unpainted white pine).

Time - (minutes) after contamination at which test is still obtainable.¹

Test Method	Contaminant		
	<u>H^{2,5,6}</u>	<u>L^{3,5}</u>	<u>HN-3^{4,5}</u>
M-6 paper	60-120	90-120	5-10
"Differential" detector			
powder	30-60	30-60	435-480
M-7 crayon mark	120-180	>480	No test
M-7 crayon paper	120-180	>480	" "
M-7 crayon powder	60-120	240-270	" "

1. A test was called negative if no appreciable color changes occurred within 5 minutes.
2. Liquid H still visible at 30 minutes; at 60 minutes, no liquid visible.
3. Liquid L rapidly absorbed; no liquid visible at 10 minutes.
4. Liquid HN-3 rapidly absorbed; no liquid visible at 10 minutes.
5. Temperature of tests using H, 35° C; using L and HN-3, 25° C.
6. C.R. paper S-328 test times: at 60 mins. - 0.2 mins., at 120 mins.-0.4 mins, at 180 mins.-1.0 mins.

TABLE 18

COMPARISON OF DETECTORS FOR GROSS SURFACE CONTAMINATION

Surface - Earth:(sandy)

Temperature - Ca. 25°C,

Time (minutes) after contamination at which test is still obtainable,¹

Test Method	Contaminant		
	H ²	L ²	HN-3 ²
M-6 paper	1-5	< 1	< 1
"Differential" detector			
powder	5-10	10-30	10-30
M-7 crayon paper	>120	>420	No test
M-7 crayon powder	>120	360-420	" "

1. A test was called negative if no appreciable color changes occurred within 5 minutes.
2. All contaminants soaked very rapidly into the earth and no liquid was visible 2-3 minutes after application.

Note: The M-7 crayon could not be used to mark the earth.

TABLE 19

COMPARISON OF DETECTORS FOR GROSS SURFACE CONTAMINATION

Surface - concrete

Temperature - Ca. 25°C

Time (minutes) after contamination at which test is still obtainable,¹

Test Method	Contaminant		
	H ²	L ²	HN-3 ²
M-6 paper	<1	<2	<1
"Differential" detector powder	<1	<2	<1
M-7 crayon mark	>240	60-90	No test.
M-7 crayon paper	>240	60-90	" "
M-7 crayon powder	>240	2-10	" "

1. A test was called negative if no appreciable color changes occurred within 5 minutes.
2. All contaminants soaked very rapidly into the concrete and no liquid was visible one minute after application.

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TABLE 20

BREAKAGE OF TUBES RESULTING FROM DROPPING OF KIT
(Drop Height ----- 4 ft.)

<u>Surface</u>	<u>Packing of Vials</u>	<u>Position of Drop</u>	<u>Tubes Broken per Drop</u>
Concrete	full*	on back face	5.4
"	"	on end	3.3
"	"	on front face	2.0
"	"	on bottom	0
"	"	on top	0
"	1/2-full**	on back face	2.5
Grass	full	"	0
Ground(hard clay)	"	"	2.3

* In full vials, contents were as follows; AC-27, CK-17, CG-17, L-17, H, HN-2 Vials of 25. Total tubes - 128.

** In 1/2-full vials, contents were as follows; AC-14, CK-9, CG-9, L-9, H, HN-2 vials of 13. Total tubes - 67.

TABLE 21

TROPICAL STORAGE LIFE OF KIT COMPONENTS

1. Carrying case	
(a) Canvas case	>6 months
(b) Metal "lift" fasteners and strap buckle	>6 months
(c) Snap hook and strap tip	badly corroded at 6 months
(d) Vial block	>6 months
2. Pump	
(a) Pump assembly	>6 months
(b) Flashlight battery	6 weeks
3. Instructions	
(a) Instruction cards	>6 months
(b) Metal binding rings	Slightly corroded at 6 months
4. Reagent containers	
(a) Bottles and rubber bulbs	>6 months
(b) Vials for solids	>6 months
5. Reagents	
(a) Caustic solution	Very heavy precipitate at 6 months but still useable for developing tests.
(b) Cupric chloride soln.	>6 months
(c) Spare reagents (solid)	>6 months
6. Detector tube containers	
(a) Plastic vials	>6 months
(b) Metal screw caps	>6 months
(c) Cellophane straws	Some straws stuck to tube at 6 months making removal slightly difficult.
7. Detectors	
(a) CK tubes	Gel assumes slight tan color at 6 months but still capable of detecting CK.
(b) AC tubes	>2 months (total time this detector has been in storage)
(c) CG tubes	4-5 months (gel assumes a green color making it impossible to detect low concentrations of CG).
(d) L tubes	>6 months.
(e) H, HN tubes	>6 months.
(1) Heaters	>6 months (efficiency, however, slightly reduced)
(f) Vesicant detector crayons	At 6 months, crumbled easily but test could be obtained if marked on paper.

TABLE 22

RESULTS OF WEARING TRIALS

1. Losses -- Of the 6 kits issued, one became lost during the operations.
2. External appearances -- Generally good, except that the canvas cases of two kits were warped due to buckling of the stiffener. In one kit, the pump-pocket flap was slightly torn.
3. Snap fasteners -- All in good working condition.
4. Pumps -- All in good working condition.
5. Internal appearances -- Generally good, except for sand found in the kits.
6. Detector tube containers
 - (a) Plastic vials -- Good.
 - (b) Metallic screw caps -- Corrosion found in approximately 30% of the caps.
7. Vial blocks -- Generally good, except that presence of sand made removal of some of the vials difficult.
8. Detector tubes - Good (none found to be broken).
9. H, HN tube heaters -- Efficiency slightly reduced (heat satisfactory but seem to react slower)
10. Liquid reagents and bottles -- Good.

APPENDIX B

Plates 1 - 15

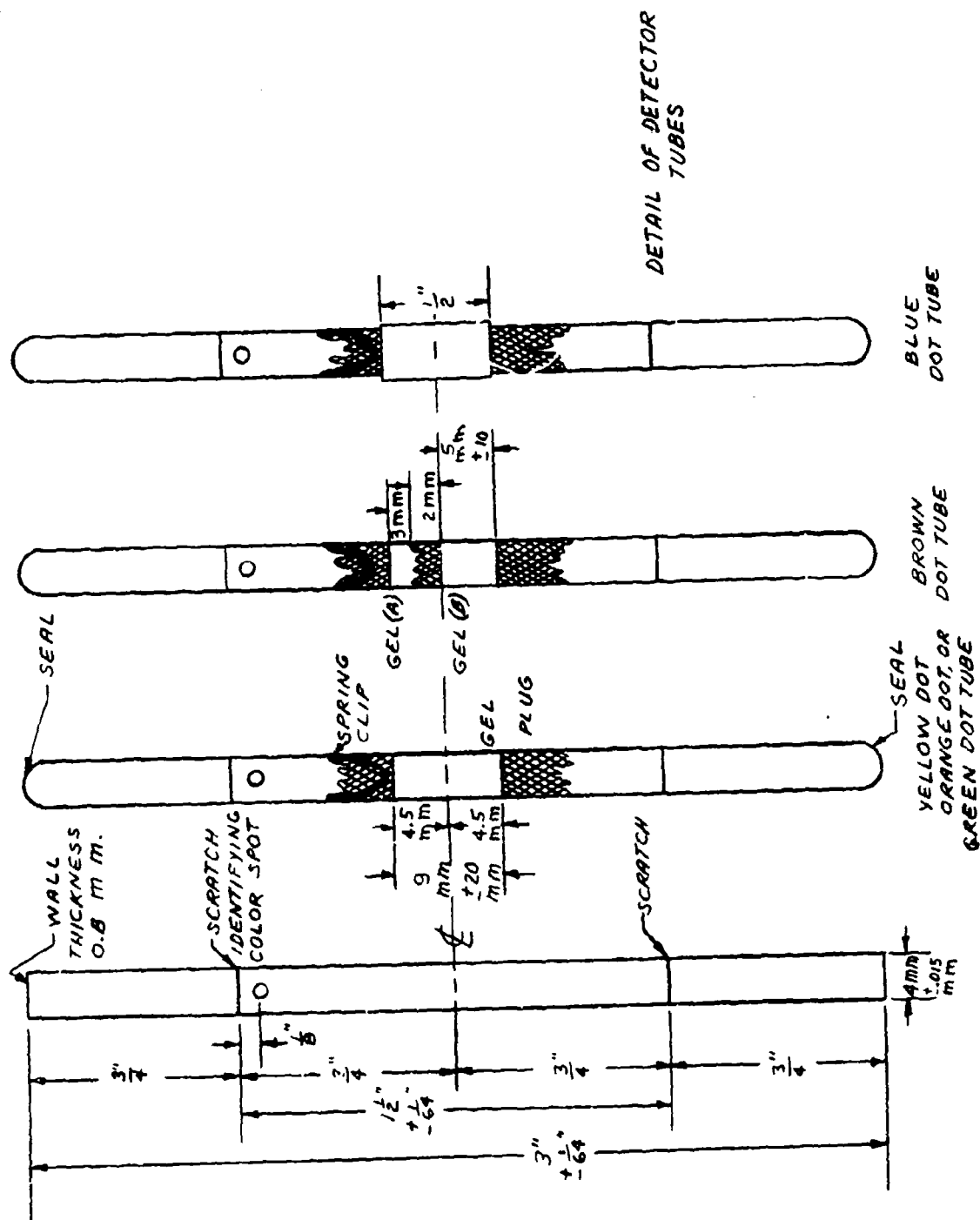
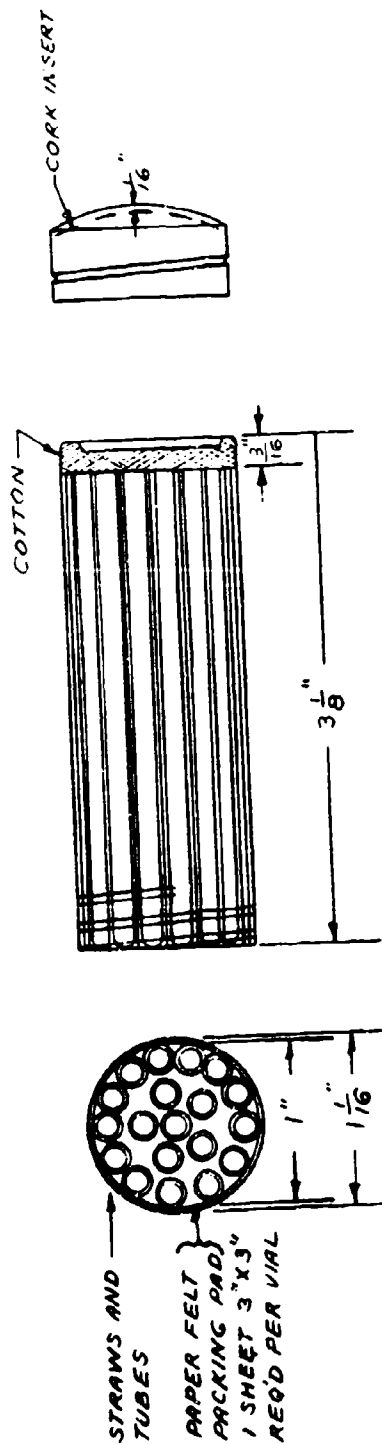
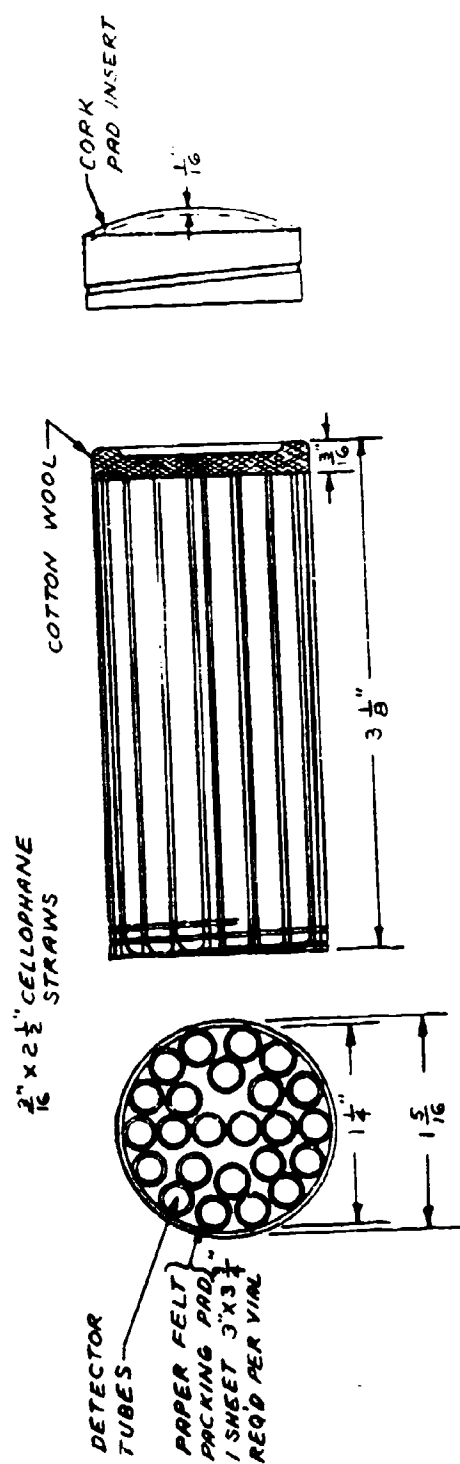


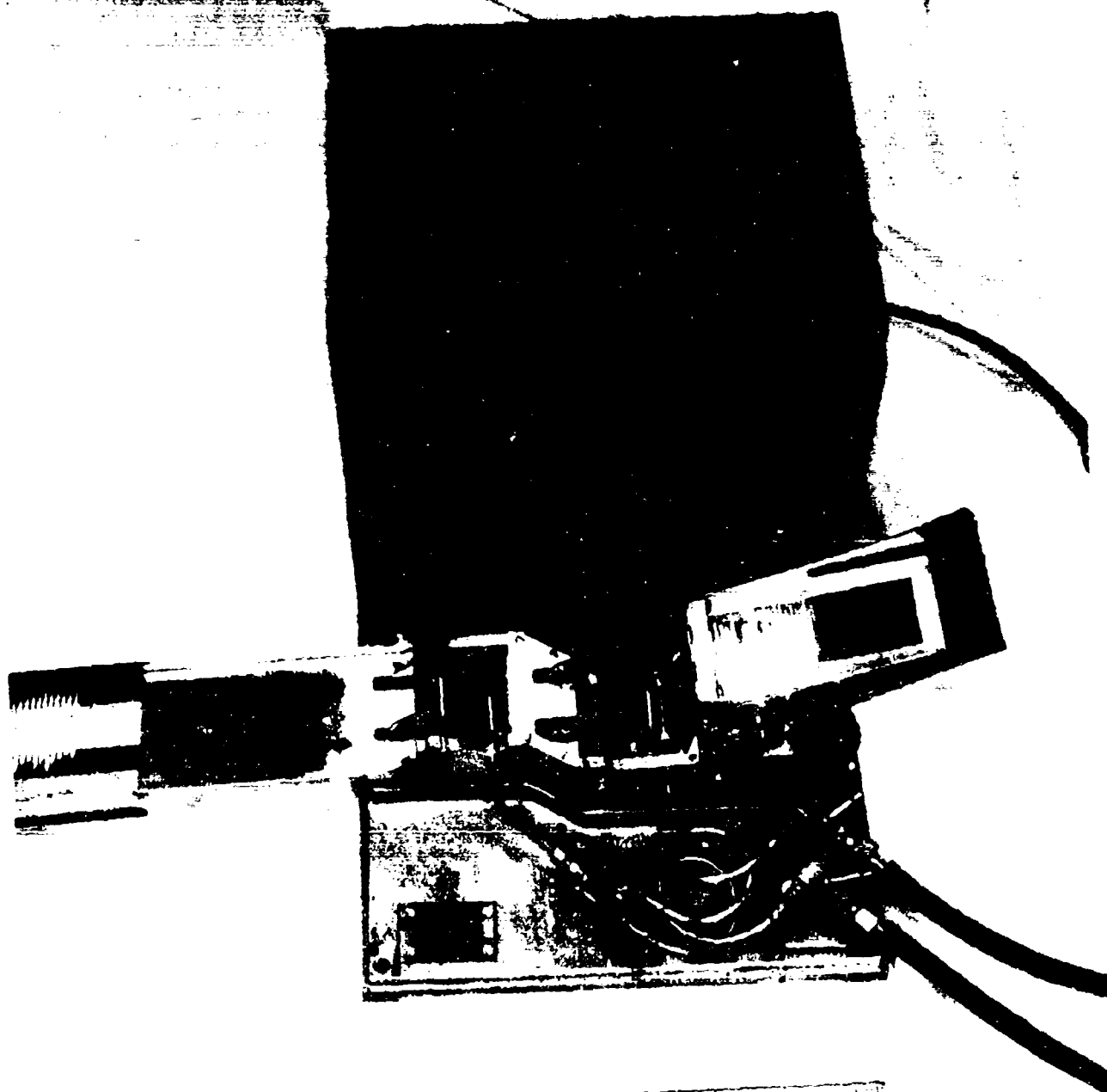
PLATE 1



DETAIL OF VIALS & PACKING



FRICTION HEATER



N.R.L. DETECTOR TUBE SEALER

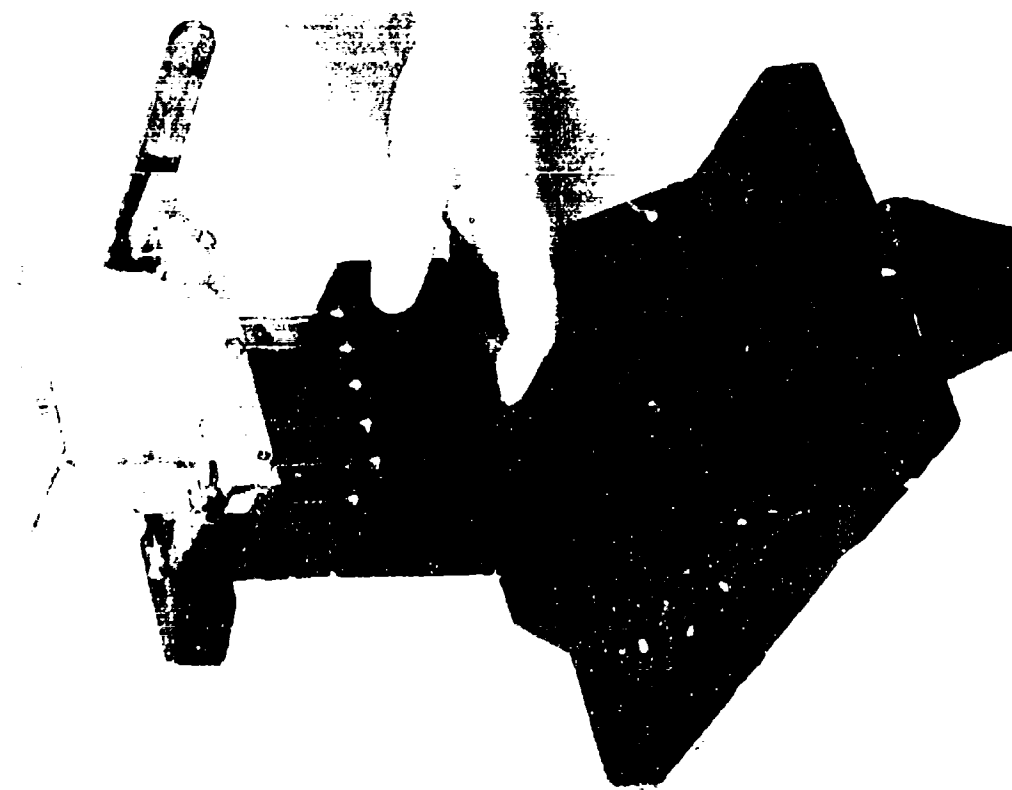


FIG. 1

M.R.L. DETECTOR TUBE FILLER

DETECTOR TUBES IN POSITION READY TO BE FILLED



FIG. 2

DETECTOR TUBES BEING FILLED



FIG. 1

TUBE-HOLDING BLOCK

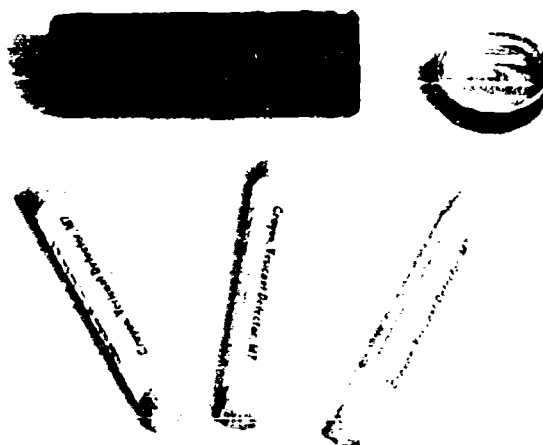


FIG. 2

M-7 VESICANT DETECTOR CRAYONS

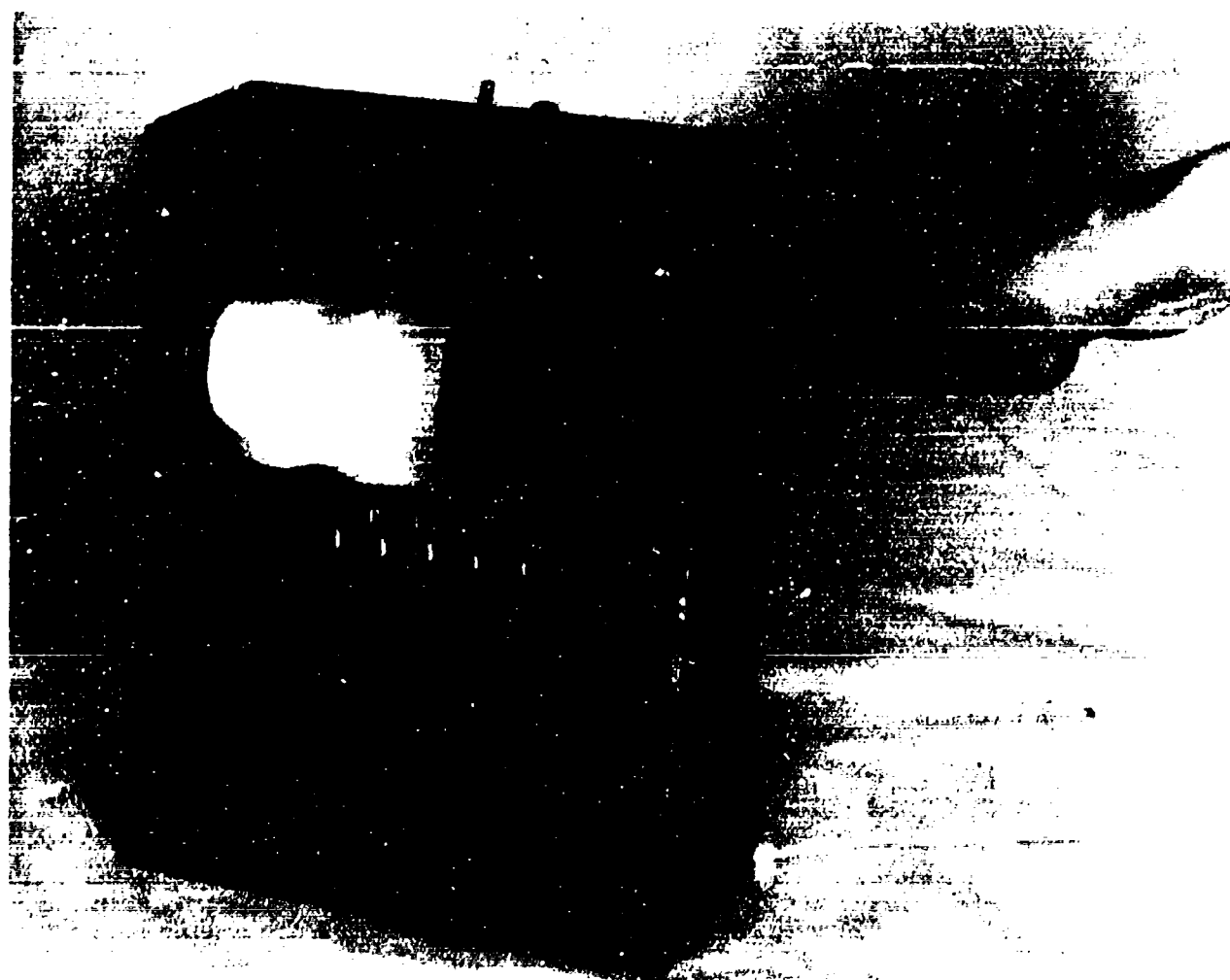




PLUG-PLUNGER & PLUG-SETTING JIG



W.R.L. PLUG-CUTTING & SETTING MACHINE



N.R.L. PLUG-CUTTING & SETTING MACHINE

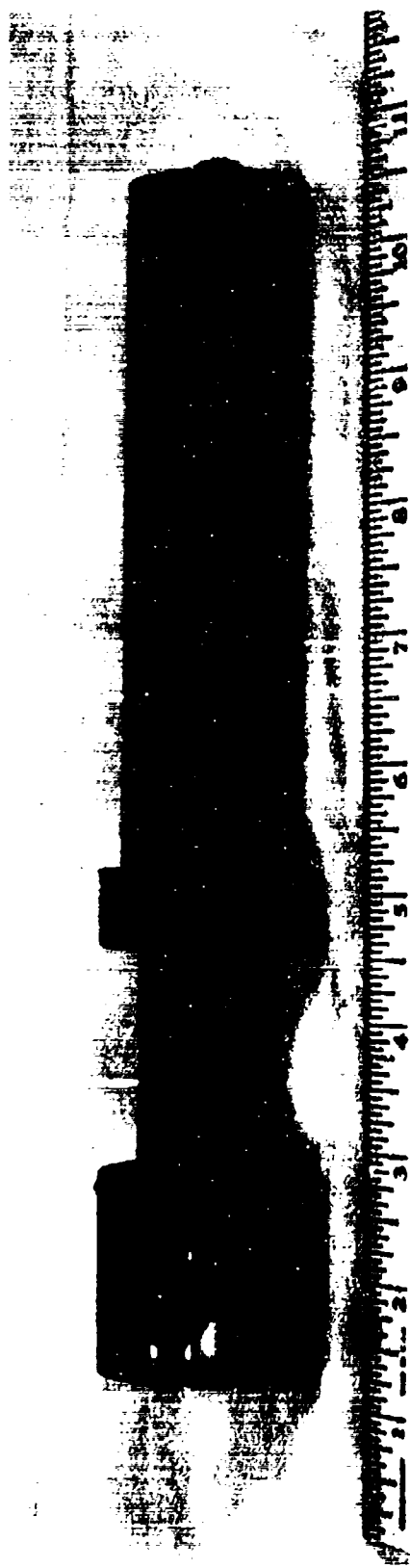


FIG. 1

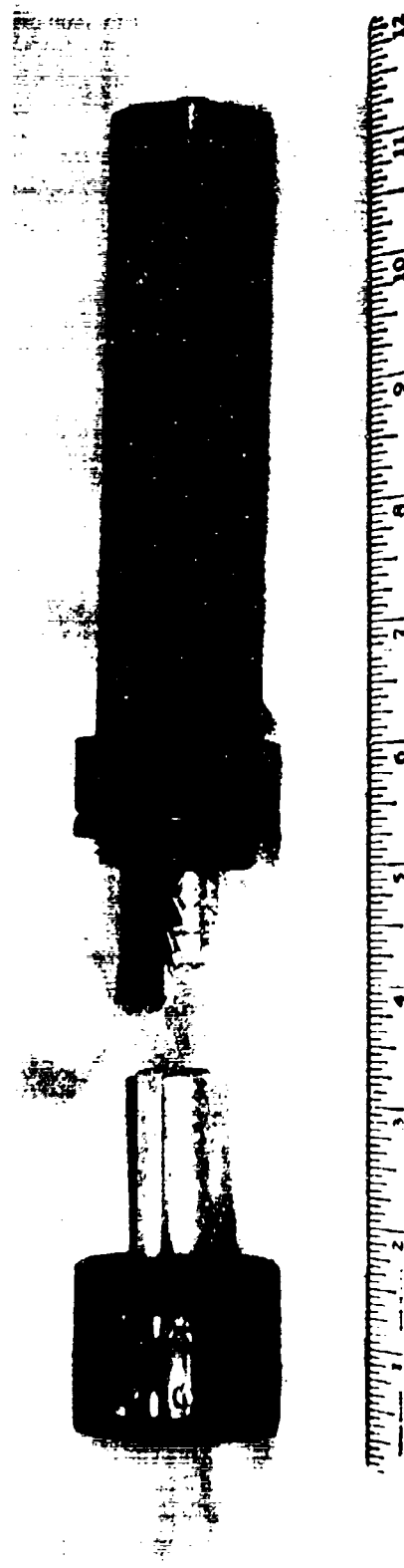
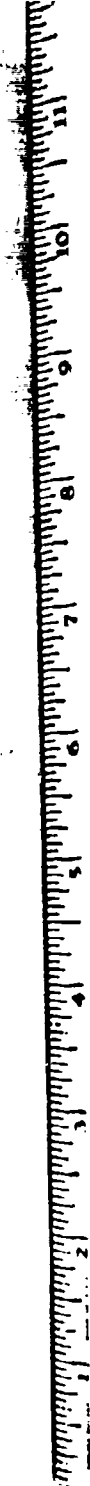
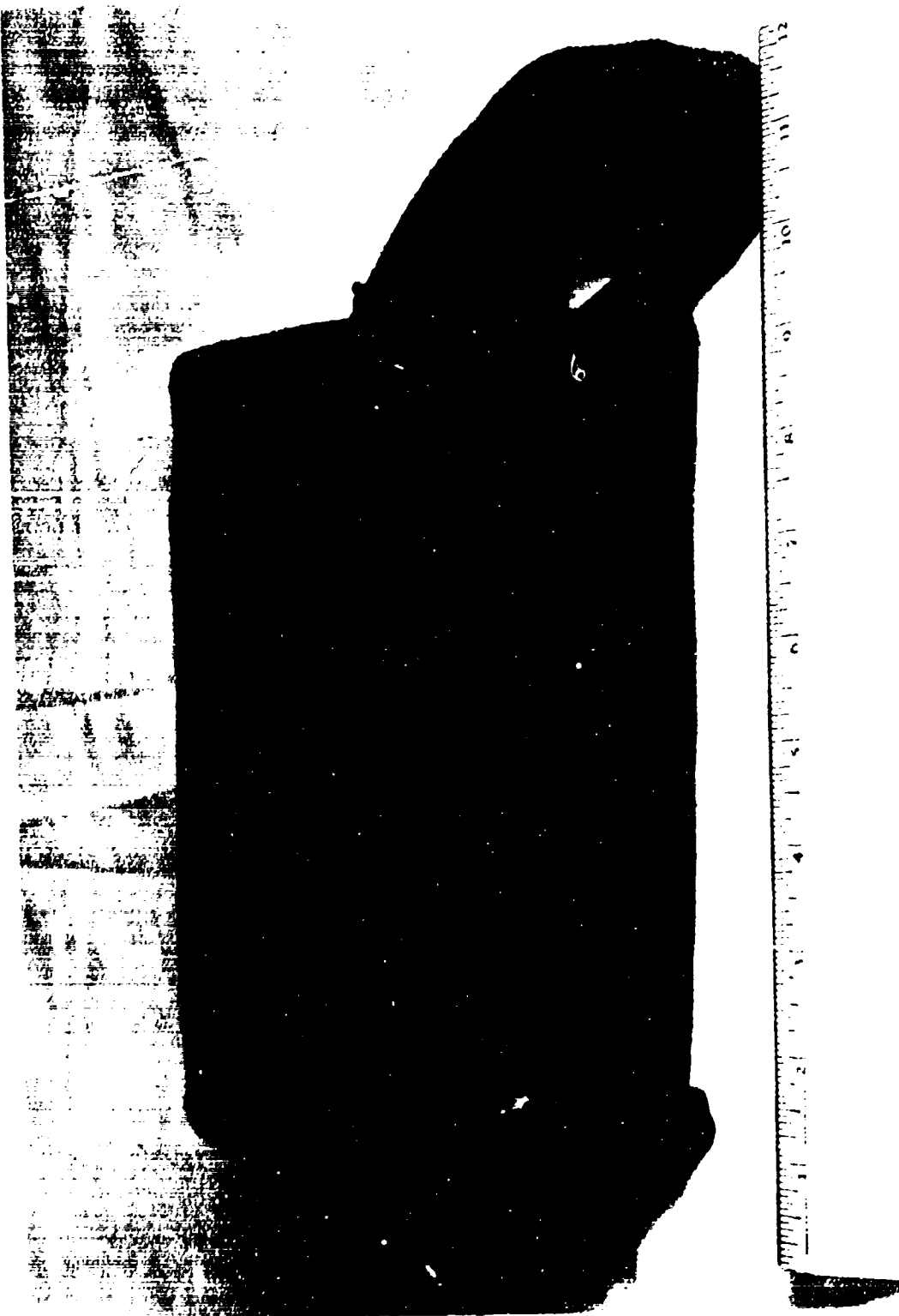


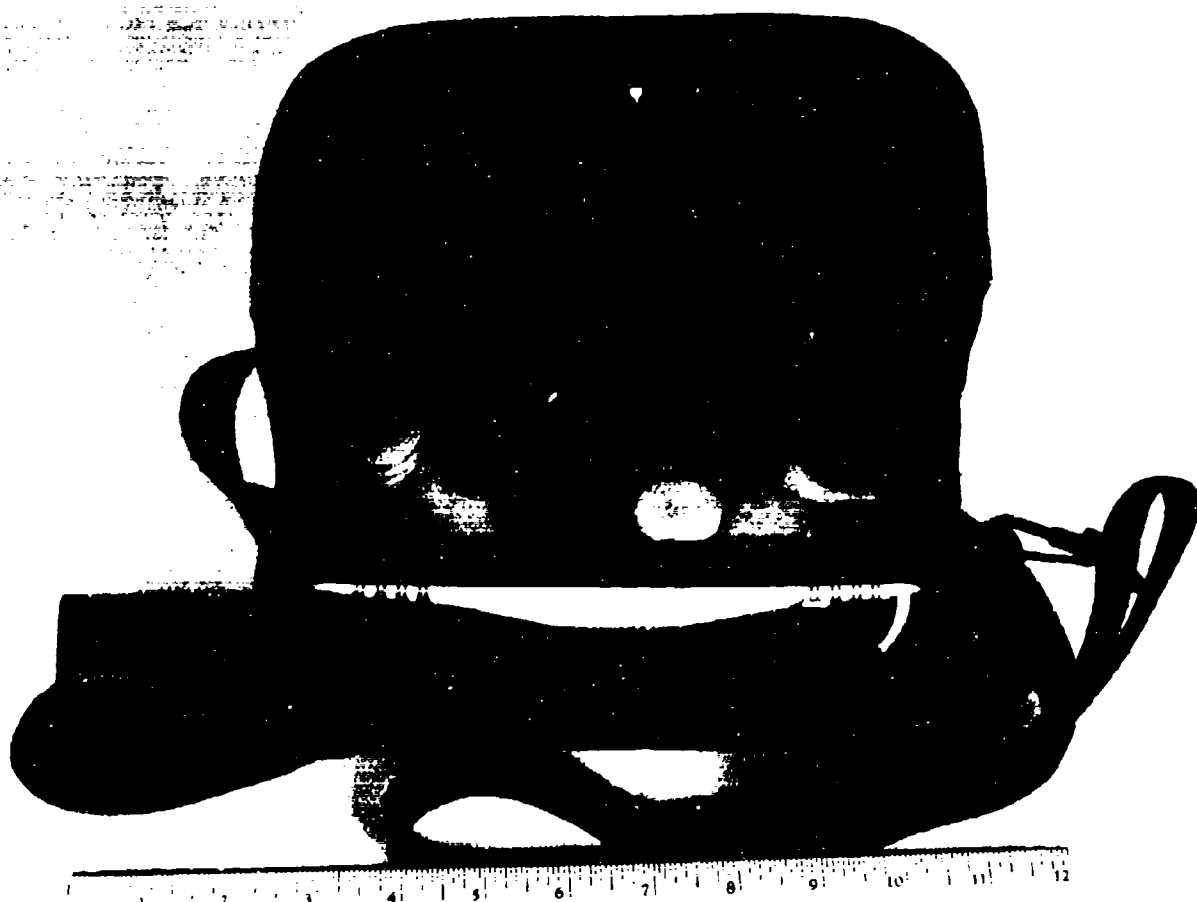
FIG. 2



VIAL BLOCK



KIT CARRIER



DETECTOR KIT (OPEN VIEW)



DETECTOR KIT (EXPANDED VIEW)

APPENDIX C

PREPARATION OF DETECTOR GELS

I. AC Detector Gel and Protective Charcoal.

A. Preparation of the Detector Gel.

1. Dissolve 7.5 g. of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in 500 ml. of distilled water. Add this solution to 500 g. of iron-free silica gel (40-60 mesh, Davison 697535 - 600 C) and stir well to obtain an even impregnation of the gel. Spread the gel in a suitable shallow dish and place in an oven. Dry for 65 hours at 105-110°C.
2. Dissolve 0.50 g. of tetramethyldiaminodiphenylmethane (TDM), and 2.50 g. of salicylic acid in 524 ml. of C.P. acetone. To this solution add 6 ml. of a 0.10% solution of TLA #35 (diazotized anthranilic acid coupled with diethyl aniline) in acetone. Add the combined acetone solutions to the copper sulfate gel prepared above and stir well to obtain a uniform impregnation. Dry the gel at 85°C for 16 hours and then at 80°C and 5-15 mm. pressure for 6 hours. The final product should be homogeneous and light-sand in color. It should be stored in a clean glass-stoppered bottle. On exposure to AC, it should change to a bright blue color.

B. Preparation of Charcoal.

3. Allow a quantity of coconut charcoal (12-30 mesh, National Carbon Co. Type G) to come into equilibrium with an air stream maintained at 80% R.H. Grind and sieve this equilibrated charcoal to a 40-60 mesh size, taking care to remove all fines. Store in a clean glass-stoppered bottle.

II. Preparation of the CK Detector Gel.

4. Dissolve 5 g. of DB3 in 550 ml. of C.P. acetone. Add this solution to 500 g. of iron-free silica gel (40-60 mesh, Davison 697535-600C) and stir well to obtain an even impregnation of the gel. Spread the gel in a suitable shallow dish and place in a vacuum oven. Dry at 55-60°C for 24 hours and then for 16 hours at 60°C and 20-25 mm.
5. Fill a glass tube (37 mm. I.D. x 36" long and tapered at the bottom to 8 mm.) to a depth of 19 cm. with the above gel. Pass a stream of pure dry air over the surface of 150 ml. of pure aniline (contained in a 500 ml. Erlenmeyer flask) and thence upward through the gel for a period of 25 minutes. The rate of flow of the air stream carrying the aniline vapor should be so adjusted that the gel is "lifted" to fill a section 30-36 cms. in length.
6. The final product should be homogeneous and white to very pale tan in color. It should be stored in a clean glass-stoppered bottle. Upon exposure to CK, an orange to red color should appear. Upon standing, this color should increase in intensity and reach a maximum about 2 minutes after exposure.

III. Preparation of the CG Detector Gel.

7. Dissolve 5 g. of p-dimethylaminobenzaldehyde, 5 g. of phenyl-naphthylamine and 0.5 g. of thiourea in 550 ml. of ethanol (95%). Add

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this solution to 500 g. of iron-free silica gel (40-60) mesh, Davison 697535 - 600 C) and stir well to obtain an even impregnation of the gel. Spread the gel in a suitable shallow dish and place in a vacuum oven. Dry at 60-65°C for 24 hours and then at 60°C and 20-25 mm pressure for 20 hours.

8. The final product should be homogeneous and golden-yellow in color. It should be stored in a clean glass-stoppered bottle. Upon exposure to CG a green color should be formed.

IV. Preparation of the L Detector Gel.

9. Dissolve 8.3 g. of $\text{Cu}(\text{NO}_3)_2 \cdot 3 \text{H}_2\text{O}$ in 550 ml. of distilled water. Add this solution to 500 g. of iron-free silica gel (40-60 mesh, Davison 697535 - 600C) and stir well to obtain an even impregnation of the gel. Dry at 95-100°C for 24 hours and then at 90-95°C and 5-15 mm. pressure for 6 hours.

10. Place one half of the above gel on a 6" Buchner funnel and pass 6 liters of a 3% KI solution through the gel over a period of one to one and one half hours. Follow this by washing with 10 liters of distilled water. Dry the impregnated gel at 90-95°C for 16-18 hours and then at 90-95°C and 5-15 mm. pressure for 6 hours.

11. The final product should be homogeneous and white to light grey-blue in color. It should be stored in a clean glass-stoppered bottle. When using this gel in a tube, the suspected air is drawn through the tube and a few drops of 10% NaOH solution are added to the exposed end. A positive test is indicated by the formation of a red to brown ring at the intake end of the gel.

V. Preparation of the Mustards Detector Gel.

12. Dissolve 5 g. of DB3 in 550 ml. of C.P. acetone. Add this solution to 500 g. of silica gel (40-60 mesh, Davison 697535-600C) and stir well to obtain an even impregnation. Spread the gel in a suitable shallow dish and place in an oven. Dry the gel at 55-60°C for 40 hours.

13. Treat the above gel with 500 ml. of a distilled water solution containing 2.5 g. of anhydrous sodium bicarbonate. Stir well to obtain a uniform impregnation. Dry at 60°C for 30 hours and then for 24 hours at 60°C and 20-25 mm. pressure.

14. The final product should be homogeneous and white in color. It should be stored in a clean glass-stoppered bottle. When using this gel in a tube, the suspected air is drawn through the tube. The tube is heated at approximately 100°C for 30 seconds and then allowed to cool. A few drops of 10% NaOH solution are then added to the exposed end. A positive test is indicated by the formation of a blue ring near the intake end of the tube. Occasionally a tan to brown color may develop. This should be ignored.

APPENDIX D

- I. TEXT OF INSTRUCTIONS.
- II. CALCULATION OF SAFE EXPOSURE TIMES TO VAPORS
OF H, HN AND L.

I. Text of Instructions.

GENERAL INSTRUCTIONS FOR USE OF KIT (page 1)

1. This kit will detect dangerous concentrations of war gases. These gases are detected by color changes in the tubes through which the suspected air has been drawn with the pump. Persistent gases detected are the Mustards (H, HN) and Lewisite (L). The non-persistent gases detected are Hydrocyanic acid (AC), Phosgene (CG), and Cyanogen chloride (CK).
2. Gas masks must be worn BEFORE this kit is used whenever the presence of a gas is suspected. The kit is then used to establish the presence or absence of a gas. When a non-persistent gas has been detected, the kit is of value to determine when it is safe to remove masks. When a persistent gas has been detected, the kit is of value to determine the length of time the contaminated area may be occupied without masks, or with masks but without protective clothing. Safe exposure times are given on pages 7 and 8.
3. Test for war gases by sampling air about 1 foot from the ground following the directions given on pages 2-6. Start with Brown Dot Tube unless a specific gas is suspected. Carry out all tests in order given.
4. Surface contamination by H or L may be tested by means of the detector crayon (page 9).

BROWN DOT TUBE (page 2)

5. Remove a BROWN DOT TUBE from the brown vial. Note that the grains are separated into a black section and a pale gray section. Snap off both ends of tube at scratches and insert dotted end into pump. Slowly take 2 full pump strokes. Examine tube. If the pale gray section turned blue, AC is present. Proceed to Orange Dot Tube (page 3).

ORANGE DOT TUBE (page 3)

6. Remove an ORANGE DOT TUBE from the orange vial. Snap off both ends of tube at scratches and insert dotted end into pump. Slowly take 2 full pump strokes. Examine tube. If an orange to red color appears, CK is present. Proceed to Green Dot Tube (page 4.)

GREEN DOT TUBE (page 4)

7. Remove a GREEN DOT TUBE from the green vial. Snap off both ends of tube at scratches and insert dotted end into pump. Slowly take 2 full pump strokes. Examine tube. If a green color appears, CG is present. Proceed to Yellow Dot Tube (page 5).

YELLOW DOT TUBE (page 5)

8. Remove a YELLOW DOT TUBE from the yellow vial. Snap off

both ends of tube at scratches and insert dotted end into pump. Slowly take 10 full pump strokes. Remove tube from pump and add liquid from Blue Bottle to undotted end of tube by means of dropper until grains are wetted. A red to brown band or ring shows L present. Proceed to Blue Dot Tube (page 6).

BLUE DOT TUBE (page 6)

9. Remove a BLUE DOT TUBE from the blue vial. Snap off both ends of tube at scratches and insert dotted end into pump. Slowly take 5 full pump strokes. Remove tube from pump and add liquid from Aluminum Bottle to cloth-heating-pad on tube by means of dropper, wetting cloth thoroughly (do not let liquid enter tube). After tube has cooled, strip off heater. Add liquid from Blue Bottle to undotted end of tube by means of dropper until grains are wetted. A blue band or ring shows H or HN present. Disregard appearance of a brown color.

SAFE EXPOSURE TIME TO VAPORS FOR MEN WITHOUT MASKS (page 7)

10. If test color is not obtained with given number of pump strokes, area is safe for men not wearing masks for the time shown in the tables below.

H or HN
use Blue Dot Tube

10 pump strokes - 1 hour
30 " " - 3 hours
50 " " - 5 hours

L
use Yellow Dot Tube

10 pump strokes - 10 minutes
30 " " - 30 minutes
50 " " - 1 hour

Note 1. Repeat tests every half hour to determine if conditions have changed. The effects of these agents are cumulative; therefore, in calculating "safe" times, total time of exposure must be considered.

Note 2. If any watering of the eyes, sneezing, or coughing occurs due to the presence of a gas, wear mask.

SAFE EXPOSURE TIME TO VAPORS FOR MEN WEARING MASKS
BUT NOT PROTECTIVE CLOTHING (page 8)

11. If test color is not obtained with given number of pump strokes, area is safe for men wearing masks, for the time shown in the tables below.

H or HN
use Blue Dot Tube

3 pump strokes - 1 hour
9 " " - 3 hours
15 " " - 5 hours

L
use Yellow Dot Tube

3 pump strokes - 1 hour
16 " " - 2 hours
24 " " - 3 hours

Note 1. Repeat tests every half hour to determine if conditions have changed. The effects of these agents are cumulative; therefore, in calculating "safe" times, total time of exposure must be considered.

Note 2. The above times may be doubled in cold or temperate climates.

INSTRUCTIONS FOR USE OF VESICANT DETECTOR CRAYONS
(page 9)

12. These crayons detect surface contamination by liquid Mustard or Lewisite, but not by Nitrogen Mustard. Best results are obtained less than 2 hours after contamination. To make test, use one of the following methods:

- (a) If surface is firm, rub crayon directly on surface. If crayon mark changes to blue within 10 minutes, surface is grossly contaminated.
- (b) Mark one side of white paper with crayon. Hold marked side directly against surface for 10 minutes. If crayon mark changes to blue, surface is grossly contaminated.
- (c) Scrape or crumble crayon into a powder and dust onto surface. A blue color, occurring within 10 minutes, indicates gross contamination.

GENERAL REMARKS (page 10)

13. In an emergency it may be necessary to replenish the liquid reagents in the Aluminum or Blue Bottles. To do this, empty contents of the same colored vial (stored in pump handle) into bottle. Add clear, unchlorinated water until bottle is 1/2 full. Shake until chemical dissolves. Fill with water (unchlorinated) and mix by shaking.

14. If dropper in the Aluminum Bottle breaks, tests can be made by pouring several drops of liquid onto cloth-heating-pad. If dropper in Blue Bottle breaks, dip undotted end of tube into liquid, remove and invert tube so that liquid wets grains.

15. A flashlight for examining tubes in the dark is provided in the pump handle.

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II. Calculation of Safe Exposure Times to Vapors of H, HN and L.

16. The safe exposure time tables found in the direction cards were calculated on the basis of the following data:

(a) Casualty data* for H and HN.

- (1) Min. casualty concentration CT = 60 (eye damage)
- (2) Min. blistering concentration .. CB = 150 - 252

(b) Casualty data for L.

- (1) Min. casualty concentration CT = 80 (eye damage)
- (2) Min. blistering concentration .. CT = 500

(c) Sensitivity data for detector tubes.

- (1) Sensitivity of H-HN detectors ... 0.5 % (table 7)
- (2) Sensitivity of L detector 6 % (table 6)

(d) Air sampled by 1 full pump stroke ... 90 ml.

17. Example calculation. Calculation of the number of pump strikes required to indicate an area safe for 1 hour, to vapors of H, for men not wearing masks.

- (a) Eye damage occurs at CT = 60 (1 %/1 for one hour).
- (b) Sensitivity of tube = 0.5 % H
- (c) 0.5 % H found in 500 ml. sample.
- (d) 500 ml. sample obtained by 5.5 pump strokes.
- (e) Using safety factor of approx. 100%, CT = 60 (1 hr.) detected by 10 pump strokes.

The other values found in the exposure time tables were calculated in a similar manner.

*Casualty data for H and HN taken from the Navy Department "Defensive Chemical Warfare Manual, FTP 222"

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