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INVESTIGATIONS ON MCE AND MFI

by

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INVESTIGATIONS ON MCE AND MFI

ABSTRACT

I. OBJECT

The object of the work described in this report was to investigate methods for the detection and identification of MCE and MFI, and to determine the resistance of various gas mask canisters to MCE.

II. RESULTS

Pure MCE was obtained from the fractionation and refractionation of the filling from 105 mm. German Grünrung III shells. The filling consisted of 20% monochlorobenzene and 80% MCE. The vapor pressure of MCE was determined at 20, 30, and 40°C. on a sample of the refractionated material. Derivatives were prepared from the agent and its reactivity to various detectors determined. Canister penetration tests were run with the agent both as a vapor and as an aerosol.

A derivative of MFI was prepared from a sample of the agent, synthesized by the NDRC. The reactivity of various detectors to MFI was determined.

III. CONCLUSIONS

It is concluded that:

A. Dimethylammonium styphnate is a satisfactory derivative for the alkylamino group and ethyl brucinium acid phosphate for the ethyl orthophosphoric acid formed on hydrolysis of MCE.

B. MCE may be detected as a molecule by the Mustards Detector of the Kit, Chemical Agent Detector, M9, if the detector is heated to 160°C. for one minute.

C. The hydrolysis products of MCE may be detected by AC detectors and by the Nitrogen Mustards Detector of the Kit, Chemical Agent Detector, M9.

D. (b)(2) HIGH

[redacted]

E. Lead isopropyl methylphosphonate is a satisfactory derivative for MFI.

F. The most sensitive detector for MFI is the Mustards Detector of the Kit, Chemical Agent Detector, M9, if it is heated to 160°C. for one minute. MFI is also detected by the Mustards Detector using the present chemical heater, but with less sensitivity.

IV. RECOMMENDATIONS

It is recommended that the Mustards Detector of the Kit, Chemical Agent Detector, M9, be modified to improve its sensitivity to MGE and MFI. This may be accomplished by developing a satisfactory method for heating the tube to at least 160°C. for one minute in the field.

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INVESTIGATIONS ON MCE AND MFI

I. INTRODUCTION

A. Object

The object of Project A10.5 was to develop and improve methods for the analysis and identification of chemical warfare agents.

The object of Project A1.13 is to investigate methods for the production, dissemination, analysis, and identification of MCE and related compounds.

The object of the work described in this report was to investigate methods for the detection and identification of MCE and MFI and to determine the resistance of various gas mask canisters to MCE.

B. Authority

This work was initiated under Project A10.5 as directed in letter SPCVR 470.6MIT(S)(1 May 1945) O-C, CWS, 1 May 1945, Subject: "Detection of Unidentified Agent in Captured Enemy Shell A10.5" to this laboratory. The work was continued under Project A1.13 upon initiation of that project by the Project Program for the Fiscal Year 1946.

II. HISTORICAL AND THEORETICAL

Ethyl diethylamine cyanophosphate, an analogue of MCE, was first prepared by Michaelis (1) in 1902. His report makes no comment on the toxic properties of the compound. Other similar compounds, dimethyl fluorophosphate (PF-2)and diethyl fluorophosphate (PF-2) were prepared by Lange and Krueger (2) in 1932.

The U.S. and British Chemical Warfare Services and the N.D.R.C. have prepared and investigated approximately one hundred and fifty analogous compounds during this war, but none was found superior to the present standard agents.

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MCE, ethyl dimethylamino cyanophosphate, was first prepared in 1937 by a German chemist, Dr. Gerhard Schrader (3, 4, 5), who turned his findings over to the German War Ministry. After an extensive investigation, the War Ministry decided to manufacture the compound on a large scale. A plant capable of producing 500 tons of the agent per month was constructed at Dyhernfurth and 12,000 tons of the agent were produced.

MFI, isopropyl methylfluorophosphonate, and a related compound, ethyl methylfluorophosphonate, were prepared by Dr. Schrader in 1938. Information on these compounds was also turned over to the German War Ministry, which investigated them. MFI was found to be the most toxic of the series of related compounds. One thousand pounds of it are reported to have been produced after serious corrosion difficulties were overcome.

MCE has been found loaded in German 105 mm. shell (Grünrung III(and in 250 kg. bombs (6, 7). No instances of any munitions containing MFI have been reported.

This laboratory was requested to investigate methods for the detection and identification of MCE and to determine the resistance of standard U.S. and foreign canisters to the agent dispersed as an aerosol. The investigation of methods for the detection and identification of MFI was also requested.

III. EXPERIMENTAL

A. Materials and Equipment

The MCE used in this investigation was obtained by the fractionation of the filling from a German 105 mm. shell (Grünrung III). The MFI was obtained from Dr. R. C. Fuson, University of Illinois. Readily available laboratory chemicals and equipment were used in this investigation.

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B. Procedure and Results

1. MCE

a. Purification

The material studied was obtained by tapping two 105 mm. German shells received at this Laboratory on 15 May 1945. Each shell contained about 1200 ml. of a dark brown, low viscosity liquid. Vacuum fractionation of the liquid from the German shells through a 1.4 cm. x 60 cm. glass Helix-packed column yielded monochlorobenzene, MCE and a dark brown residue. The ratio of MCE to monochlorobenzene was approximately 5:1. Data on the fractionation and two refractionations of the material are given in Tables I and II.

Analyses were carried out on the crude shell filling for cyanide, total nitrogen, phosphorus and chlorine content, and on purified MCE for cyanide, total nitrogen, and phosphorus. These data are given in Table III.

b. Vapor Pressure

Vapor pressure measurements were made on a sample of re-fractionated MCE by a modification of the dynamic method of Baxter, Bezzenberger, and Wilson (8). Nitrogen, dried over anhydrous calcium sulfate, was metered by a Rotameter at a rate of 500 ml./min., through two weighted Geissler tube saturators in series, maintained at constant temperature in a water bath. The loss-in-weight data from the saturators containing the MCE were converted to vapor pressure at the three temperatures measured with the following results:

Temperature (°C.)	Vapor Pressure (mm. Hg)
20	0.038
30	0.097
40	0.210

These values were calculated using 162 as the molecular weight of MCE.

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TABLE I

FRACTIONATION OF MATERIAL FROM GERMAN SHELL

	1st Fraction	2nd Fraction
Distillation temperature	43°C/8-9mm.	90-93°C/6mm.
Jacket temperature	75°C	110-125°C
Pot bath temperature	90°C	140-160°C
Charge	658 g.	
Recovered	128 g.	305 g.
Residue		214 g.(34.3%)
Recovery	19.4%	46.3%
Loss		0.15%

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TABLE II

RE-FRACTIONATION OF MCE FROM GERMAN SHELL

	1st Re-Fractionation	2nd Re-Fractionation
Distillation temperature	76-78°C/2mm.	78-80°C/2 - 3mm.
Jacket temperature	110-115°C	115°C
Pot bath temperature	120-130°C	120-125°C
Charge	54 g. water-white agent	36.8 g.(bp.76-78°C/ 2mm. - distillate from 1st Re-Fractionation)
Recovered	48 g. water-white distillate	33.0 g. water-white distillate
Residue**	4.5 g.	2.8 g.
Recovery	88.8%	89.7%
Residue (%)	8.3%	7.6%
Loss and hold-up	2.9%	2.7%
Time required (hours)	2	2 1/2
*n_D^{25} before Re-Fractionation	1.4226	1.4224
*n_D^{25} immediately after Re-fractionation	1.4224	1.4226
*n_D^{25} 64 hours after Re-fractionation	1.4224	

* Same operator and same instrument used in all measurements.

** Residue was not a tar but was material which remained in flask after the Re-Fractionation. It was slightly discolored where the glass wool was in contact with the walls of the pot.

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TABLE III

ANALYSIS OF GERMAN SHELL FILLING

(b)(2) HIGH

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c. Derivatives

(1) Dimethylammonium Aurichloride

Four-tenths of a milliliter of pure MCE was added with stirring to a solution of 1.0 g. of chloroauric acid in 2 ml. of distilled water. The mixture was stirred until all agent had dissolved and then allowed to stand and crystallize. The crystals were collected on a filter and then dryed at 65°C. The crude product melted 192-196°(corr.) (literature m.p. 195-8°).

The crude dimethylammonium aurichloride was recrystallized by solution in absolute ethanol followed by precipitation with anhydrous ether. No improvement in melting point was obtained. Recrystallization by solution in acetone and precipitation with isopryopyl ether or solution in isopropanol and precipitation with isopropyl ether also failed to improve the melting point.

The data in Table IV were collected to prove that the alkylamino group in the German MCE is dimethylamino. Authentic samples of dimethylammonium aurichloride and diethylammonium aurichloride were prepared from dimethylamine hydrochloride and diethylamine hydrochloride.

(2) Dimethylammonium Styphnate

Seven-tenths of a milliliter of pure MCE was added to a solution of 1.0 g. of styphnic acid (2,4,6-trinitroresorcinol) in 10 ml. hot ethanol. The compound separated as long yellow prisms on cooling. After recrystallization from ethanol, the compound melted 209.5-210.5°(corr.)(literature m.p. 208°(9)).

No depression in melting point was obtained with a sample of derivative prepared from dimethylamine hydrochloride. Diethylammonium styphenate, prepared from diethylamine hydrochloride, melted 136-137° (corr.) after recrystallization from a mixture of benzene and ethanol.

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TABLE IV

MELTING POINTS OF AURICHLORIDES

Material	Melting Point (°C. Corr.)
diethylammonium aurichloride	178-180
aurichloride from MCE	192-196
dimethylammonium aurichloride	192-196
mixed m.p. of dimethylammonium aurichloride with aurichloride from MCE	191-193
mixed m.p. of diethylammonium aurichloride with aurichloride from MCE	below 150

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Microanalysis of a sample of the derivative prepared from MCE gave the following results:

	Calc'd. for $C_8H_{10}O_8N_4$	Found
%C	33.1	33.6,33.7,34.1
%H	3.45	3.46,3.52,3.56
%N	19.3	19.22,19.24

(3) Ethyl Dibrucinium Phosphate

This derivative was prepared from MCE by several procedures, the most satisfactory of which was the following: Four-tenths of a milliliter of MCE was added to a hot solution of 1.0 g. of brucine in 15 ml. of acetone. Two milliliters of distilled water containing five drops of concentrated hydrochloric acid were then added to the mixture. On standing and cooling, the derivative separated from solution as long colorless needles. It was collected on a filter and washed with acetone. After two recrystallizations from a 5:1 benzene-ethanol mixture, the derivative melted 90-93°(corr.). When mixed with samples of the derivative prepared from ethyl orthophospheric acid and from ethyl ammonium phosphate, no depression in melting point was observed.

The following results were obtained on analysis of the derivative:

	Calc'd.for $C_{48}H_{59}O_{12}N_4P$	Calc'd.for $C_{48}H_{59}O_{12}H_4P.3\ H_2O$	Found
%C	62.9	59.4	60.1,60.4,57.16,57.59
%H	6.45	6.72	6.79,7.10
%N	6.12	5.78	5.80,5.79,5.58,5.57
%P	3.39	3.20	3.3,3.31

(4) Ethyl Brucinium Acid Phosphate

This derivative was prepared by recrystallizing a pure sample of ethyl dibrucinium phosphate from isopropanol. It was purified by further recrystallization from isopropanol to give colorless crystals, m.p.203-205°C.

This melting point is obtained if the sample is inserted in the melting point bath at 100°C. or lower and heated to the melting point from that temperature. If the sample is inserted above 125°C., it melts immediately. This behavior may be due to loss of isopropanol of crystallization during the slow heating. Microanalysis of the derivative gave the following results:

	Calc'd. For $C_{25}H_{33}O_8N_2P$	Calc'd For $C_{25}H_{33}O_8N_2P.C_3H_7OH$	Found
%C	57.7	57.8	56.6;56.5
%H	6.34	7.07	6.98,7.13
%N	5.38	4.83	4.83 (4.67,4.73)

d. Detection

Various standard U.S., British, and German agent detectors were tested against the filling from the German shell and against the purified agent. Paper, Liquid Vesicant Detector, M6, AC-CK Detector Tube, MIT-E26R14, the Navy AC Detector, and the Nitrogen Mustard Detector of Kit, Chemical Agent Detector, M9 gave tests with either the shell filling or the purified agent. In addition, a positive test is obtained with the German Black Band Tube which would ordinarily be used for the detection of AC. The experimental data are presented in Table V.

Sensitivities to MCE of the AC-CK Detector Tube (MIT-E26R14), the Navy AC Detector Tube, the German AC Detector Tube, the Nitrogen Mustards Detector tube as well as the Mustards Detector from the Kit, Chemical Agent Detector, M9, the last heated to 160°C. for one minute were determined at 10, 50 and 85% relative humidity in air and at zero and 50% relative humidity in nitrogen using the standard sensitivity apparatus (10). In estimating the concentrations, the volatility of MCE was taken as 0.28 mg/l/ at 25°C. The data are given in Table VI. The results of these experiments indicate that the MCE is hydrolyzed in moist air to produce AC and an alkaline material, probably dimethylamine. The experiment also indicates that the AC detectors are not detecting the agent itself, but hydrolysis products. The Mustards

Detector from the Kit, Chemical Agent Detector, M9, heated to 160°C. for one minute appears to be the only detector giving a test for the agent as a molecule. The data indicate piperidine to be a more sensitive developing agent than 10% aqueous sodium hydroxide for the tube heated to this temperature.

e. Canister Penetration Tests

(1) MCE Vapor Penetration

Canister penetration tests were run at approximately 0.5 mg./l. MCE concentration at 32 l./min. constant flow rate. This agent concentration was generated by passing the entire airstream through a 6-inch column of the MCE. The standard AC indicator used in canister testing (See Table VII) was used half strength at 1 l./min. flow rate. The data from these tests are given in Tables VII and VIII.

(2) MCE Aerosol Penetration

An aerosol of MCE was generated by passing the agent through an aspirator, C.W.S. Drawing No. E21-47-23, into an air stream. The aerosol was then passed into the canister at a rate of 32 l./min. and the penetration measured by means of an Optical Smoke Meter MIT-E1R3. The canisters were measured for Methylene Blue Smoke penetration before and after exposure to the MCE smoke. The concentration of agent was approximately 100 micrograms /l. as determined by measuring the weight increase of a Gooch crucible after having passed a known volume of the air mixture through it. The particle size of approximately one to two microns was measured on a clean glass slide by means of an ocular micrometer on a microscope. The data collected during these tests are given in Tables IX - XII.

2. MFI

a. Derivative

Lead isopropyl methylphosphonate was prepared by adding 1 ml. of MFI (with stirring) to a hot

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TABLE V

REACTIVITY OF VARIOUS DETECTORS TO PURIFIED MCE

1. U. S. Detectors

Paper, Liquid Vesicant Detector, M6.	Positive test with liquid, olive green to red.
Crayon, Vesicant Detector, M7.	No change.
M9 Kit detector tubes.	No change except following hydrolysis of the agent under neutral or alkaline conditions, or in humid air, whereupon a positive test was obtained with the Nitrogen Mustards Detector.
Mustards Detector of M9 kit heated to 160°C for one minute.	Positive test with vapor.
Ag-CK Detector Tube, E26R14.	Positive test (light blue to pink) over pure agent or following hydrolysis, particularly after acid (3N H_2SO_4) hydrolysis; after alkaline hydrolysis (1% NaOH) the intensity of color change was reduced.
Metanil Yellow/$HgCl_2$ type AC detector tube.	Positive test, orange to purple; effect of alkaline hydrolysis not as marked as above.
Navy AC Detector Tube.	Positive test, light blue to dark blue; effect of alkaline hydrolysis not as marked as on AC-CK Detector.

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TABLE V (continued)

2. British Detector Papers

"Spotted Dick" type.	No Change.
"Iodoplatinate" (AIP) type.	No Change.

3. German Detector Tubes.

Tube Marking	Type	Color Change Produced by Above Agent
1 yellow band	H and arsine	None
2 yellow bands	HN	None
1 green band	CG	None
2 green bands	PS, CK and oximes	None
1 black band	AC	Light grey to green-blue.

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TABLE VI

ESTIMATED SENSITIVITIES OF AC, AND DB-3 DETECTORS TO MCE

(At 10, 50, and 85% Relative Humidities in Air and At 0 and 50% Relative Humidities in Nitrogen)

Sensitivities Expressed in γ of MCE

	Atmosphere of Nitrogen		Atmosphere of Air		
Detector	Dry	50%	10%	50%	85%
AC-CK Detector Tube MIT, E26R14	No Test	15-22.5	18-22	5-6	18-23
Navy AC Detector Tube	"	9-12	3-4	9-13	10-14
German AC Detector Tube	"	1.5-3	2-3	2-3	2-3
Nitrogen Mustards Detector Tube (M9 Detector Kit)	"	1.5-3	3-5	3-5	6-8
Mustards Detector Tube (DB-3) (M9 Detector Kit) Heated 1 min.at 160 C. Developed with Piperidine	6.8-8.1	6.8-8.1	4.1-5.4	5.4-6.8	5.4-6.8
Mustards Detector Tube (DB-3) (M9 Detector Kit) Heated 1 min at 160 C. Developed with 10% NaOH	18.9-20.3	18.9-20.3	16.2-17.6	17.6-18.9	17.6-18.9

[redacted]

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TABLE VII

GAS PENETRATION TESTS OF M11 and M10A1 CANISTERS WITH MCE

Concentration+	approximately 0.5 mg./l. generated by passing 32 l./min. of air through a six-inch column of MCE at room temperature
Flow rate	32 l./min.
Relative humidity	50 percent
Condition of canisters	Dry (as received)
Indicator	Half strength AC indicator, (TDMR 753, "The Technic and Chemistry of Canister Testing") used at 1 l./min. flow rate. This indicator is sensitive to the order of magnitude of 5γ of the compound.

	Canister life in minutes	
	M-11 Canister	M10A1 Canister
Crude MCE shell filling	(b)(2) HIGH	
Pure MCE fraction		

+ - Concentration estimated by measuring weight loss of a Geissler tube saturator containing pure MCE through which measured quantities of dry Nitrogen were passed at room temperature.

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TABLE VIII

MCE GAS PENETRATION OF JAPANESE SERVICE CANISTERS

MCE Concentration	- Approximately 0.5 mg./l
Flow Rate	- 32 l./min.
Relative Humidity	- 50 percent
Penetration indicators	- Navy AC detector tube Five (5) white mice. +

Japanese Canister	Canister Life in Minutes
Navy Model 93-2	(b)(2) HIGH
Army Model 95	
Army Model 99 (1940)	
Army Model 99 (1943)	
Army Model 99 (1944)	

\+ Mice placed in atmosphere of the canister effluents for the duration of each test suffered no observable ill effects.

++ At the end of 30 minutes there was an amine-like odor in the canister effluent, and the Nitrogen Mustards Detector tube (acid-base indicator) of the M9 Kit gave a positive test for a basic material.

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TABLE IX

MCE PENETRATION OF FILTERS MEASURED WITH OPTICAL SMOKE METER MIT-E1R3

Particle Size - Approximately 1-2 microns
Concentration - Approximately 100 micrograms/liter
Flow Rate - 32 l/min.
Relative Humidity - About 50%

Time (mins)	Percent Penetration					
	Smoke from Purified MCE			Smoke from Crude MCE		
	M-11	M10A1 Carbon Paper	Canadian Mark I	M-11	M10A1 Carbon Paper	Mark I
1	(b)(2) HIGH					
3						
5						
7						
9						
11						
13						
15						

[redacted]

[redacted]

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TABLE X

METHYLENE BLUE PENETRATION DATA BEFORE AND 20 HOURS AFTER EXPOSURE OF CANISTERS TO MCE SMOKE UNDER CONDITIONS STATED IN TABLE IX

Time of Methylene Blue Smoke Test	Percent Methylene Blue Smoke Penetration					
	Canisters Tested with Pure MCE			Canisters Tested with Crude MCE		
	M-11	M10A1 Carbon Paper	Canadian Mark I	M-11	M10A1 Carbon Paper	Canadian Mark I
As Rec'd.	0.005	0.025	0.025	0.005	0.025	0.0075
20 hrs. after MCE Test	0.005	0.011	5.70	0.005	0.09	3.30

[redacted]

[redacted]

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TABLE XI

MCE PENETRATION OF JAPANESE FILTERS MEASURED WITH OPTICAL SMOKE METER MIT-E1R3

Particle Size - Approximately 1 micron
Concentration - Approximately 130 micrograms/liter
Flow Rate - 32 l./min.
Smoke Generated from crude MCE shell filling.

Time (min)	Percent Penetration (b)(2) HIGH
1	
3	
5	
7	
9	
11	
13	
15+	

+ For the duration of each test, the canister effluent was passed through a bottle containing a white mouse. There was no noticeable effect on the mouse in any case.

[redacted]

[redacted]

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TABLE XII

METHYLENE BLUE PENETRATION DATA BEFORE AND 20 HOURS AFTER EXPOSURE OF JAPANESE CANISTERS TO MCE SMOKE UNDER CONDITIONS STATED IN TABLE XI

Time of Methylene Blue Smoke Test	Percent Methylene Blue Smoke Penetration				
	Navy Model 93-2	Army Model 95	Army (1940)	Model 99 (1943)	(1944)
As Received	0.025	0.08	0.45	0.11	0.075
20 hrs. after test MCE	0.02	0.08	0.40	0.11	0.08

[redacted]

suspension of 1.85 g. of lead oxide in 10 ml. of distilled water. After cooling, the lead fluoride and the excess of lead oxide were removed by filtration. The derivative was isolated by concentrating the filtrate to 1 - 2 ml. It was then collected on a filter and dried. After two recrystallizations from benzene containing a few drops of ethanol, the derivative melted 136.5-137.5°(corr.).

Microanalysis of a sample of the derivative gave the following results:

	Calc'd. for $C_8H_{20}O_6P_2Pb$	Found
%C	20.0	20.00, 20.38
%H	4.17	4.11, 4.11
%Pb	43.0	42.6, 41.5, 41.7, 42.1

b. Detection

Various standard U.S., British, and German vapor detectors were tested against the vapors over a bottle of MFI in an effort to find a detector for the agent. The detectors investigated are listed in Table XIII. The Mustards Detector Tube in the U.S. Kit, Chemical Agent Detector, M9, was the only standard detector which gave a positive test with MFI. The Drake fluorine detector (11) also showed a positive test with the agent.

Sensitiveness to MFI of the Drake Fluorine detector, the Mustards Detector from Kit, Chemical Agent Detector, M9 heated in the normal manner and the Mustards Detector heated to 160°C. for one minute, were determined at 10, 50, and 85% relative humidity in air and at zero and 50% relative humidity in nitrogen using the standard sensitivity apparatus (10). The volatility of MFI was taken as 14.64 mg./l. at 25°C.(12). The Mustards Detector heated to 160°C. was found most sensitive. Data are shown in Table XIV. The same values were observed in dry and in wet nitrogen, showing that the agent is not being detected as a hydrolysis product.

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TABLE XIII

DETECTORS TESTED AGAINST MFI*

1. M9 Mustards Detector
2. M9 Nitrogen Mustards Detector
3. M9 Arsenicals Detector
4. M9 Phosgene Detector
5. SeO_2 Arsenicals Detector
6. $PdCl_2$ Arsenicals Detector
7. AC-CK Detector
8. DNDB-3 Mustards Detector
9. $HAuCl_4$ Mustards Detector
10. British S.D. Paper
11. British A.P.I. Paper
12. German Mustard Detector
13. German Nitrogen Mustard Detector
14. German Phosgene Detector
15. German Chloropicrin Detector
16. German AC Detector

*Note positive test was obtained with Mustards Detector, [redacted] Chemical Agent Detector, M9.

The German Nitrogen Mustards Detector turned from yellow to orange. A red color denotes Nitrogen Mustards.

Since the data in Table XIV showed the Mustards Detector to be more sensitive to MFI when heated to 160°C., as did the data in Table VI with MCE, work was initiated toward finding a simple method for obtaining such a temperature in the tube in the field. By modifying the present aluminum foil heater of the Mustards Detector to include a layer of aluminum foil beneath the webril as well as above it and using a 50% aqueous sodium hydroxide solution instead of saturated cupric chloride for heat development, it has been found possible to produce temperatures of 150-160°C. in the tubes. Temperatures of 170-200°C. were obtained with a mixture of nitrocellulose and hexamethylenetetramine applied to the tube and ignited by a safety match head imbedded therein. This work was discontinued before completion due to the ending of development at this Laboratory.

IV. DISCUSSION

Material from two 105 mm. German shells (Grünrung III), on vacuum fractionation yielded monochlorobenzene, MCE, and a tarry residue, probably the decomposed agent. No attempt was made to obtain further products than the chlorobenzene and MCE from the shell filling. Analyses of the shell filling (see Table III) show it to be composed of 20% monochlorobenzene and 80% MCE.

The vapor pressure of MCE was determined on a sample of the German material after re-fractionation. A limitation must be placed on the accuracy of these measurements. Although efforts were made to exclude water vapor from the system, it is possible that enough penetrated the apparatus to hydrolize the quantity of agent that was volatilized by the nitrogen. If this hydrolysis had taken place with subsequent volatilization of additional quantities of the agent, the results could be high. One measurement which was made in an air bath, with little chance of water contamination, fell approximately on the curve for the points determined in a water bath. It is believed, therefore, that the results are sufficiently accurate for all practical purposes.

TABLE XIV

ESTIMATED SENSITIVITIES OF DB-3 AND DRAKE'S FLUORINE DETECTOR TO MFI
At 10, 50 and 85% Relative Humidities in Air and at 0% and 50%
Relative Humidities in Pure Nitrogen
(Sensitivities expressed in γ of MFI)

	Atmosphere of Nitrogen		Atmosphere of Air		
Detector	Dry	50%	10%	50%	85%
* Drake's Fluorine Detector	175	105	60	95	29
DB-3	115	115	240	115	145
DB-3 (heated at 160°C)	19	19	29	19	19

Concentration of Agent, MFI, was 107 gamma per liter, based on Volatility Data. All sampling was done by means of an M9 Kit Pump. (Pump capacity assumed to be 90 ml.)

* See OSRD Report No. 4843, 19 April, 1945, Pg. 19

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Because of the probable difficulty of preparing a derivative of the entire molecule, an effort has been made to prepare derivatives of the hydrolysis products. Dimethylammonium curichloride and dimethylamino styphnate were prepared as derivatives of the dimethylamino group. Both are easily prepared from the agent in good yield. Dimethylammonium styphnate is considered the better derivative as it is more easily purified and not hygroscopic. The picrate was not considered as a possible derivative because the melting points of dimethylammonium picrate and diethylammonium picrate are in too close a proximity to each other and thus MCE would be difficult to distinguish from the corresponding ethyl diethylamino cyanophosphate.

The brucine salts, ethyl dibrucinium phosphate and ethyl brucinium acid phosphate, were prepared as derivatives of the ethyl orthophosphoric acid formed by hydrolysis of MCE. Both derivatives are easily formed. The ethyl brucinium acid phosphate appears to be somewhat more easily purified to give a satisfactory melting point.

MCE was found to give positive tests in air containing as little as 10% relative humidity with the MIT-E26R14 AC Detector, the Navy AC Detector, the German AC Detector, the Nitrogen Mustards Detector, and the Mustards Detector from the Kit, Chemical Agent Detector, M9, the last when heated to 160°C for one minute. In dry nitrogen, only the Mustards Detector gave a test. Sensitivity values for these detectors were determined and are included in Table VI. These data indicate that in the case of the AC detectors and the Nitrogen Mustards Detector, the agent is being detected only in the form of its hydrolysis products.

MCE was tested as both vapor and aerosol against the M-11, M10A1, Canadian Mark I, Japanese Navy Model 93-2, and the Japanese Army Model 95 and 99 (1940, 1943 and 1944) canisters. The data in Tables VII and VIII show that the M-11, M10A1, Japanese Navy Model 93-2, and the several Japanese Army Model 99 canisters all have adequate protection for 30 minutes. As an additional

[redacted]

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(b)(2) HIGH

MFI was treated with lead monoxide in the same manner as in the preparation of derivatives of PF-1, PF-3, diethyl fluorophosphate, and dicyclohexyl fluorophosphate, to give lead isopropyl methylphosphonate as a derivative. The compound is easily prepared and purified and has a sharp melting point in the desired temperature range.

Of the agent vapor detectors tested against MFI, the Mustards Detector from Kit, Chemical Agent Detector, M9 and the Drake fluorine detector (11) were the only ones found to give a positive test with the agent. The sensitivity data presented in Table XIV show the Mustards Detector from Kit, Chemical Agent Detector, M9, to be the most sensitive detector for the agent if heated to 160°C. for one minute. The Drake fluorine detector is not believed sufficiently sensitive to the agent to warrant the use of an apparatus so heavy, bulky, and difficult to handle.

Both MCE and MFI are satisfactorily detected by the Mustards Detector of Kit, Chemical Agent Detector, M9, if the tube is heated to 160°C. for one minute instead of with the present chemical heater. Therefore, a field method for obtaining such a temperature in the tube is believed desirable. Work was initiated toward that end, but no completely satisfactory method was developed before work was stopped.

[redacted]

V. CONCLUSIONS

It is concluded that:

A. Dimethylammonium styphnate is a satisfactory derivative for the alkylamino group and ethyl brucinium acid phosphate for the ethyl orthophosphoric acid formed on hydrolysis of MCE.

B. MCE may be detected as a molecule by the Mustards Detector of the Kit, Chemical Agent Detector, M9, if it is heated to 160°C. for one minute.

C. The hydrolysis products of MCE may be detected by AC detectors and by the Nitrogen Mustards Detector of the Kit, Chemical Agent Detector, M9.

D. (b)(2) HIGH

E. Lead isopropyl methylphosphonate is a satisfactory derivative for MFI.

F. The most sensitive detector for MFI is the Mustards Detector of the Kit, Chemical Agent Detector, M9, if it is heated to 160°C. for one minute. MFI is also detected by the Mustards Detector using the present chemical heater, but with less sensitivity.

VI. RECOMMENDATIONS

It is recommended that the Mustards Detector of the Kit, Chemical Agent Detector, M9, be modified to improve its sensitivity to MCE and MFI. This may be accomplished by developing a satisfactory method for heating the tube to at least 160°C. for one minute in the field.

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INVESTIGATIONS ON MCE AND MFI

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