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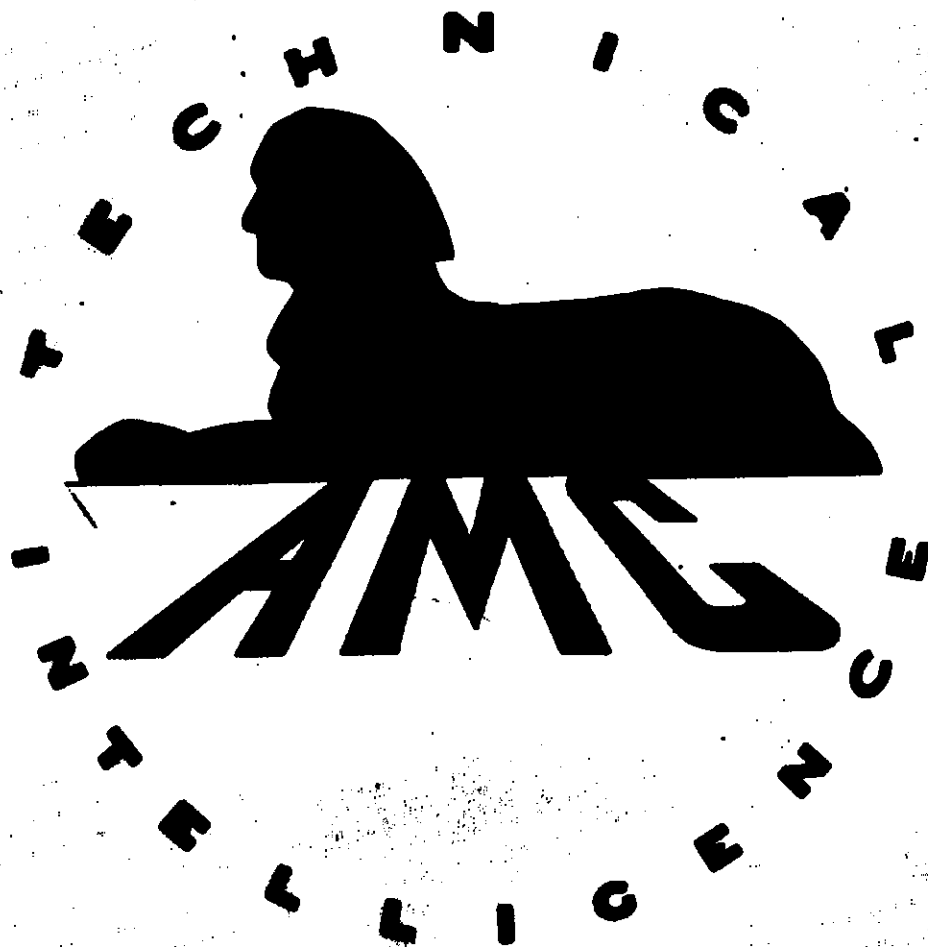
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NATIONAL DEFENSE RESEARCH COMMITTEE

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POLAROGRAPHIC ANALYSIS OF PRIMERS

by
James J. Lingane

Report C D No. 4881
Copy No. 52
Date: March 30, 1945

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POLAROGRAPHIC ANALYSIS OF PRIMERS

Ssrvice Project: OD-118

Endorsement from Dr. Ralph Connor, Chief, Division 8 to
Dr. Irvin Stewart, Executive Secretary of the National Defense
Rssearch Committee.

Forwarding report and noting:

"This report describes a technique whereby very small amounts
of mixtures of inorganic compounds commonly found in primers
and dotonators can be analyzed quantitatively by means of
the polarograph. It has been shown in OSRD 4564 that the
polarograph is not generally adaptable for use with mixtures
of organic nitro compounds; nevertheless, it is believed that
the use of the polarograph, especially in conjunction with a
qualitative microscopic examination as described in OSRD 3757,
constitutes a feasible laboratory method for the analysis of
certain ammunition components. The procedure is capable of
further refinement and probably is capable of extension to
include other ingredients, but it is believed that adaptation
of this technique to specific Ordnance problems can best be
made by the Arsenals using the fundamental work herein de-
scribed as a background. Consequently, polarographic work
on this type of material has been terminated by NDRC."

This is the final report under Contract OEMsr-1028 with Harvard
University.

POLAROGRAPHIC ANALYSIS OF PRIMERS

This project was undertaken to develop polarographic methods[1]

---

(1) I. M. Kolthoff and J. J. Lingans, "Polarography", Interscience
   Publishers, N. Y. (1941)

---

of analysis for primers, primer detonators, and the materials used
in their manufacture. Since these mixtures vary widely in their
composition and nature, we confined our investigations to a typical
mixture composed of potassium chlorate, cuprous thiocyanate,
antimonoue sulfide (stibnite), lead azide, and mercury fulminate.

All materials used in this investigation were either of
reagent grade or of Ordnance quality; most of the samples were
obtained from Picatinny Arsenal through the courtesy of the
Commanding Officer. Analyses were performed wherever it was thought
desirable; the results of these analyses and other pertinent data are
listed in Table I:

Table I. Analysis of Materials Used

Substance	Specification	Analysis
Antimonous sulfide	50-11-14B	97.5% theoretical Sb
Mercury fulminate	50-11-6B	101.2% theoretical Hg
Lead azide	50-13-12A	99.6% theoretical Pb, 100% N_3
Cuprous thiocyanate		prepared in this laboratory by reduction of reagent $CuSO_4$, precipitation with KCNS, washing with dilute H_2SO_3, acetone and ether. Air dried, see text.
Sodium azide	E. K. Co. technical	Recrystallized, see text.

The mercuric fulminate was analyzed by dissolving a weighed
sample in 2 M ammonium acetate on the steam bath, diluting to a known
volume, and recording the polarograph.

The stibnite was analyzed by dissolving in concentrated
hydrochloric acid, boiling to remove hydrogen sulfide, dilution to a

volume of 100 cc., which was 1 M in free hydrochloric acid, and recording the polarograph. The sulfide was determined using the method outlined in this report.

Analysis of the lead azide for lead content was made in the same manner as that for mercury in mercuric fulminates.

The azide ion was determined cerimetrically. A sample of lead azide was allowed to stand in a known volume of standard ammonium hexa nitrato cerate overnight, an excess of potassium iodide was added, and the liberated iodine titrated with standard thiosulfate solution.

Azide Ion

A sample of technical grade sodium azide was purified by preparing a saturated aqueous solution, precipitation with a large volume of pure ethanol, washing and drying in a vacuum desiccator.

Solutions of sodium azide were investigated in various supporting electrolytes. No indication of reduction at the dropping mercury electrode was observed in 0.1 M potassium nitrate, 0.001 M hydrochloric acid, nor in 0.1 M hydrochloric acid plus 0.2 M potassium chloride. According to Latimer[2] the reversible potential for the reduction of

---
(2) W. M. Latimer, "Oxidation Potentials", Prentice-Hall, Inc., New York (1938).
---

hydrazoic acid to ammonium ion is +0.41 v., and for its reduction to ammonium ion and nitrogen is +1.57 v. vs. the saturated calomel electrode. Since in spite of these strongly oxidizing reversible potentials no reduction wave was found at the dropping electrode it seems that the reduction requires a larger activation energy than can be obtained in this manner.

It was found that the azide ion produced an anodic (oxidation) wave in potassium nitrate supporting electrolyte at the dropping electrode. In those experiments a saturated mercurous sulfate electrode was employed, and care was taken to avoid traces of chloride ion which produces a similar anodic wave, which would interfere. The anodic wave of azide ion starts at a potential of +0.15 v. vs. the saturated calomel electrode. At small concentrations the wave con- sists of two parts, but with larger concentrations a third wave appears. Measurements of the anodic diffusion current just prior to the dissolu- tion of mercury show that it is proportional to the concentration up to about 2.5 millimolar, but above this point the limiting current remains constant and almost independant of azide concentration. From the similar behavior of the halides[1] we believe the anodic reaction to be

$$2Hg + 2N_3^- = Hg_2(N_3)_2 + 2e \qquad (1)$$

The diffusion current constant, $i_d/(Cm^{2/3} t^{1/6})$, determined with concentretions of azide ion from 0.85 to 2.38 millimolar is 2.45 ± 0.07 at 25° in 0.5 M potaesium nitrate. According to Equation 1 one equivalent of electricity is involved per mols of azide ion. This fact, coupled with the above value of tha diffusion current constant givas a diffueion coefficient for azide ion of 1.55×10^{-5} $cm^2 sec^{-1}$, which correeponds to a value of 58 $ohms^{-1}$ for tho equivalent conductance.

Ths anodic wavo wae investigated also in 0.5 M sodium acetate, ammonium acctate, acetic ecid, sodium acotate plue ecetic acid, and aodium tartrate plue tartaric acid. In all thesa casee aither no wava was observed or elee it was inferior to that obsarved with potassium nitrate ae supporting electrolyte.

To obtain mora information on whether the wave was due to the depolarization of the dropping electrode with the formation of ineoluble mercuroue azide (Equation 1) or to the actual oxidation of thd azide ion, the behavior of azide ion war investigated with a etationary platinum micro-electrode.[1] This electrode consisted of a bright platinum wire 0.7 mm. in diameter eealed in ths and of a soft glass tube with 3.5 mm. exposed. The elsctrode wae oleaned in chromio acid and handled with the utmoct care. The readings wero made manually 20 minutes after each change in the applied voltage, to allow time for a steady etate of diffueion to be reached. The wave thus obtained starts at about +0.85 v. and ie fairly well developed. There ie no doubt that thie wave is due to oxidation of azide ion to nitrogen (bubblee of gas were notod on the electrode) according to

$$2N_3^- = 3N_2 + 2e \qquad (2)$$
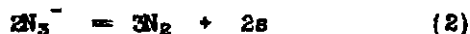
Since the anodic wave of azida ion at the platinum electrode occure at a potential that is about 0.8 v. moro poeitive than that at the dropping mercury electrode, and since thero ie no reason to believe that the overvoltage at the platinum anode ie any greater than at the mercury surface (if anything it should be smaller), it ie clear that tho reaction at the mercury electrode cannot be the oxidation of the azide ion, but must be due to tho oxidation of the mercury itself according to equation 1. Alternatively, tha reaction might bo aesumed to be the formation of mercuric azide or an azido-marcuric complex, but we belisve that aither of theee poesibilitiea is lass probable than equation 1.

Anodic wavae wore also obtainsd at the platinum micro-cloctrode from ammonium acstete as supporting electrolyte. In oither ammonium acetate or potaeeium nitrate the wavs occure at a potential sufficiently poeitive eo that oxygen (air) need not be removed. Although potaeeium nitrate ia a better supporting electrolyte than ammonium acetate, it ie not ao auitable for use in the practical analyeis of primers. Since ammonium acetate would be e good extractant for lead azide in primers we have ueed it to determine the relation between the

limiting current and the concentration of azide ion. Table II contains representative data obtained with the platinum enode.

Table II
Limiting Current and Concentration of Azide Ion at 25°
in 0.5 M Ammonium Acetate

NaN₃, millimolar	i_d, microamp.	i_d/C
0.769	3.2	4.2
1.48	6.5	4.4
2.14	9.2	4.3
2.76	12.4	4.3
3.08	13.5	4.4
4.33	19.1	4.4

These values were measured at +1.1 v. $\underline{ve}$. the seturated celomel electrode, and are corrected for the residual current. The ratio i_d/C decreeeas significantly with concentrations much larger than 3 or 4 millimolar. With very large concentrations of azide ion the current fluctuotee erratically. The accuracy with which azide ion can be datarminad by thie technique ie ebout ± 5%. Each electrode must be calibrated with known concentrations of azide ion.

Dilute perchloric acid was aleo tried es a supporting electrolyte and gave results better than ammonium acatate and about the same ae potaseium nitrate. Some typical data are ehovn in Tabla III.

Tob. III
Limiting Anodic Current and Concentration of Azide Ion
at 25° in 0.05 M Perchloric Acid with a Platinum Microelectrode

NaN₃, millimolar	i_d, microamp.	i_d/C
0.769	2.30	2.99
1.48	4.30	2.91
2.91	8.35	2.86
5.62	15.6	2.78
8.15	20.7	2.54

From the above it oan ba seen that the platinum microelactroda servee fairly well for the dstermination of azide ion in oither potaseium nitrate, perchloric acid, or ammonium ecetate media, but only the latter two have much eignificance in practical analyeis of primers. They should both eerve as extractants of lead azids, but ammonium acetate would probebly be a better choice than parchloric acid becauee the latter might diesolve appreciable amounte of antimony sulfide which ie aleo present in acme primar mixturee. It will be nacsseary to calibrnte the alactrode with known amounte of azide ion et the eame time thet the analyais is

performed, since we have noted that the values of i_d/C obtained with
the same electrode are subject to change with use of that electrode.
The accuracy obtainable should be well within ± 10%, which perhaps will
serve for practical analysis. There is also a possibility that the
method can be improved with experience.

Sulfide Ion

Sulfide ion produces a well-defined anodic wave with the dropping
mercury electrode in alkaline medium. We have found that in the absence
of antimony the diffusion current of sulfide ion is directly propor-
tional to the concentration up to about 1.25 millimolar. With larger
concentrations the value of the diffusion current is relatively too
small. A somewhat similar effect is observed in the case of the halide
ions, and in this particular case is probably due to the deposition of
a film of the insoluble mercuric sulfide on the dropping electrode.

It was observed that the presence of antimony decreases the
diffusion current of the sulfide wave, although it has no effect on the
shape. When stibnite is dissolved in a solution of potassium tartrate
and potassium hydroxide (4 M potassium hydroxide plus 2 M potassium
tartrate, the anodic sulfide wave is well defined, but the cathodic
antimony wave is not. A peculiar hump was also noted just prior to
the antimony wave. This was not accidental, for it was observed in all
our experiments. Solutions of "synthetic" stibnite, formed by adding
stoichiometric amounts of potassium antimonyl tartrate and sodium
sulfide to the alkaline tartrate electrolyte showed the same unfortunate
characteristics, so they cannot be due to the natural material itself.
Since either ion produces an excellent wave by itself in this medium the
observed behavior must be due to their simultaneous presence. It was
noted that solutions of stibnite in the alkaline tartrate medium slowly
deposit a dark precipitate on standing a few hours. Polarographic
analysis of this residue indicates that it contains antimony. Table IV
shows the effect of antimony on the sulfide wave.

Table IV
Influence of Antimony on Anodic Diffusion Current of Sulfide Ion
in 0.25 M Potassium Hydroxide, 0.125 M Potassium Tartrate, 0.005%
Gelatin (Sulfide as Sodium Sulfide, Antimony as Potassium Antimonyl Tartrate

$S^=$, millimolar	Sb^{+++}, millimolar	$i_d/(Cm^{2/3}t^{1/6})$ sulfide ion
0.587	0.000	3.78
0.565	0.196	3.52
0.546	0.383	3.38 (= Sb_2S_3)
0.528	1.29	3.08
0.510	2.14	2.91

From the above results it appears reasonable to believe that in

an alkaline tartrate solution containing both antimony sulfide part of
the sulfide exists in s complex with the antimony. In the absence of
sulfide the antimony is possibly present as a hydroxy-tartrato complex,
but when the sulfide is edded it apparently replaces part of the
hydroxy or tertrato groups, so that there then existe a hydroxy-
tertrato-sulfido complex. Such a complex would undoubtedly give e
"sulfide" wave, but since the size of such s complex is much greater
than that of the sulfide ion, its diffusion current constant is much
smaller. Therefore the existence of such e complex would account for
the anomalous behavior we have observed. Our experiences thus far led
us to eecertain whether the diffusion current is proportional to the
concentration of sulfide ion when the ratio of sulfur to antimony is
constant. In many experiments s fair proportionality was observed,
but difficulties, later traced to air oxidation of the sulfide,
convinced us that attempts to determine sulfide in the presence of
antimony were not profitable, and we abandoned this line of endeavor.

Lead, Mercury, and Antimony Ions

Previously published investigations[3] have shown that the wave

(3) J. J. Lingans, Ind. Eng. Chem., Anal. Ed., 15, 583 (1943).

of + 3 antimony precedes that of l. d in 1 N hydrochloric acid, but
that in 1 N sodium hydroxide the c.der is revareed. Both waves are
well defined in both media, and are directly proportional to the con-
centration over the entiro practical polarographic range. The
simultaneous polarographic determination of these two metals presente
no problem. If tha lead predominatee an acid medium is called for,
and vice versa. Good waves ere also obtained in alkaline tartrate;
the lead wave comes first and again both aro well defined. Satis-
factory waves are also obtained in 1 N nitric acid.

Mercury producee a good wave which in all ceeas starts from
zero applied voltage. This wave is well defined, and proportional
to the concentration over the range of the method.

Cupric Ion

The cuprous thiocyanate used in this investigation wee prepared
in this laboratory. It was analyzed by the iodometric method and was
found to contain 96.4% of the theoretical amount of coppar.

It was found that 50 mg. of this material would not dissolve in
e convenient volume (50 cc.) of 2 M ammonium acetate or potassium
nitrate. It war found that the addition of oxidizing egents increesee
the solubility markedly, and 30% hydrogen peroxida was finally choeen,
since any excess could be conveniently boiled off without contamination
of the solutions.

Lingane[4] hae previously reported ths behavior of the cupric-

(4) J. J. Lingane, J. Am. Chem. Soc., **65**, 866 (1943).

tartrate complex. In an acid tartrate medium one well-defined step is obtained, while in basic tartrate e doublet ie found. Neutral tartrate also gives e eingle wave. In ammonia-ammonium chloride a doublet is obtained, but in ammonium acetete - acid tartrate mixtures only a single wave ie observed.

Summary of Polarographic Characteristics

The half-wave potentiale and the diffueion current constants of the chief metallic conetituente of primers were determined in various supporting electrolytee. Using these values concentrations can be found directly from meesured diffusion currents and the known values of $\underline{m}$ and $\underline{t}$ for the electrode.[3] Table V lists the data. All half-wave potential values are referred to the eeturated calomel electrode, diffueion currente were measured at 25.0° C, and 0.01% of gelatin was preeant in all supporting electrolytes es a maximum suppressor.

Table V. Polarographic Constants of Primer Metale

Supporting Electrolyte	$E_{\frac{1}{2}}$, volts				$i_d/(Cm^{2/3}t^{1/6})$			
	Sb	Cu	Pb	Hg	Sb	Cu	Pb	Hg
1 M HCl	-0.15	+0.04 -0.22	-0.43		5.54	3.39	3.86	
0.3 M Zn(NO₃)₂ + 1 M HNO₃			-0.025	-0.40	--		2.34	3.50	2.67
1 M NH₃ + 1 M NH₄Cl		-0.24 -0.50				3.75		
0.4 M sodium tartrate + 0.1 M eodium hydrogen tartrate	-0.80	-0.09	-0.48		3.40	2.37	2.37	
0.5 M eodium tartrate	-1.0	-0.12	-0.50		3.90	2.24	2.30	
0.5 M eodium tartrate + 0.1 M NaOH	-1.32	-0.10 -1.30	-0.75		3.54	--	2.39	
1 M HCl + 0.3 M KCl + 0.2 M terteric acid	-0.16				4.56			
1 M NH₄Cl + 1 M acetic acid + 1 M HCl		-0.26 -0.40	-0.45	--	3.20	3.71	3.84	
1 M ammonium acetate + 0.4 M eodium tartrate + 1 M eodium hydrogen tartrate		-0.19	-0.50			2.52	2.71	

General Plan of Analysis

We first sought to separate the various components from mixtures preliminary to polarographic analysis. These mixtures were made by weighing out known quantities of potassium chlorate, stibnite, lead azide, mercury fulminate, and cuprous thiocyanate. Separation of the stibnite was effected by extraction with ammonium acetate containing a small amount of hydrogen peroxide, which dissolved everything except the stibnite.

The residue of stibnite is dissolved in an alkaline tartrate solution, the solution is then acidified strongly with hydrochloric acid, and the hydrogen sulfide evolved is absorbed in an excess of a standard iodine solution, which is finally back-titrated with standard thiosulfate solution. The residual acid solution in the still is diluted to a known volume, and its antimony content is determined polarographically.

As a result of much trial and error the apparatus shown in Fig. 1 was finally developed for the sulfide determination. The 50-cc. flask (A) has two side tubes, one for the slow stream of purified nitrogen which is swept through the system constantly to prevent air oxidation and the other to serve as a reservoir for the concentrated hydrochloric acid used to evolve the hydrogen sulfide from the dissolved stibnite. Since antimony trichloride is appreciably volatile at temperatures in the neighborhood of 100° C., the flask was fitted by a ground joint to the condenser (B). The hydrogen sulfide is collected in a 250-cc. bottle, fitted with a gas-lift type bubbler tube (C), which contains the standard iodine solution. As a supplementary absorber the outlet from this bottle is passed into a test-tube (D) which contains a few cubic centimeters of dilute potassium hydroxide. Before titration of the excess iodine the contents of (D) are added to (C). Table VI gives the results for the determination of sulfur in several stibnite samples.

Table VI
Determination of Sulfur in Stibnite

Stibnite mg.	Sulfide recovery %
18.2	98.0
28.4	94.1
21.2	96.0

That the average recovery of sulfur in stibnite is several per cent low is not surprising. Experiments have shown that the samples we used contained about 2% of material insoluble in the alkaline tartrate solution (probably siliceous material), a small amount of lead (probably as galena), and a small amount of iron. If this last is
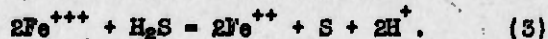
JJL OEMsr-1028
9-15-44
FIG.2

FIG 1

JJL
OEMsr-1028
5-15-44
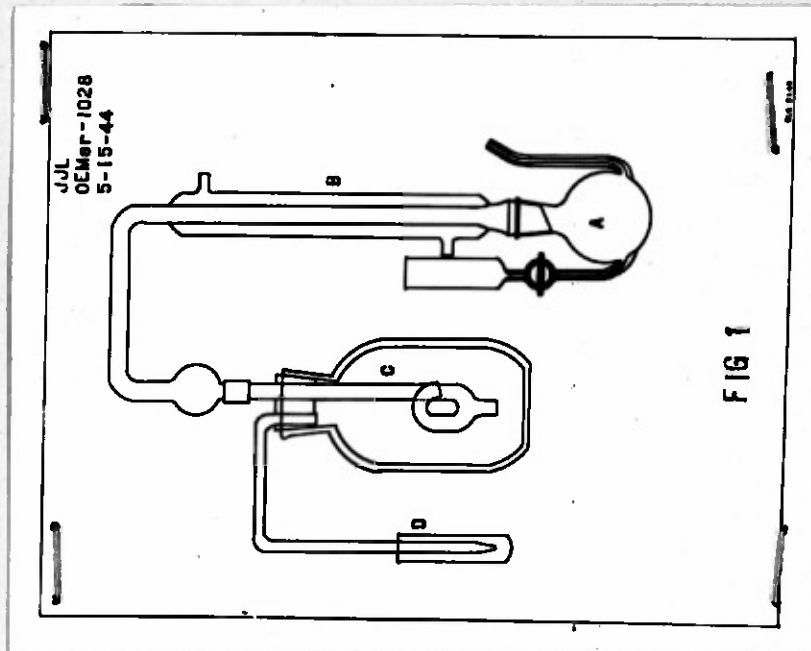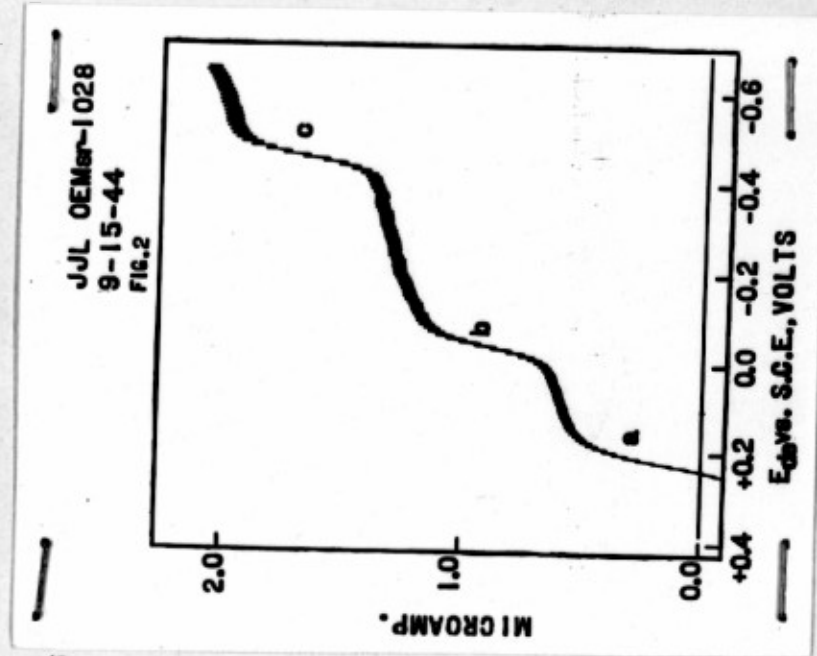
preeent in the ferric etate it will cause low results for sulfur
when tho eample ie aoidified due to the reaotion,

$$2Fe^{+++} + H_2S = 2Fe^{++} + S + 2H^{+}. \qquad (3)$$

Small deposits of free sulfur were noted on the inner tube of the
oondeneer from this reaction.

The simultaneous determination of meroury, copper, and lead was
first attempted by direct polarography of the ammonium aoetete extraot
from whioh the etibnite had been eeparated. Resulte were diecouragingly
low, and addition of eodium tartrate plus eodium hydrogen tartrate did
nct improve them. Experiments with tho metale individually pointed to
mercuric fulminate ae the eource of difficulty, apparently through
eome oxidation produot of the fulminate ion. Attempte to recover the
metale by a sulfide preoipitation and subeequent eolution with nitric
ecid were aleo unsatisfaotory. It wae finally deoided to attempt to
recover the free metele from the extract by plating them out on a metel
more baee than any ordinarily encounterod in Ordnance material. Zinc
wae choeen eince ite wave occure at a potential considerably more
negative than those of the other metals. The plated zinc can bo die-
eolved in nitric acid, and, after eluting to a known volume the mer-
oury, lead, end copper in this solution cen be determined eimultaneouely
from a single polarogram. That thie procedure ie eotiefeotory is
indicated by the reculte shown in Table VII.

Table VII. Recovery of Known Metal Samples by Zinc Plating Method

Metal taken, mg.	Metal found, mg.	Recovary, %
Hg 14.1	Hg 14.1	100.0
Cu 0.34	Cu 0.34	100.0
Pb 11.6	Pb 11.6	100.0
Hg 20.2	Hg 20.00	99.0
Cu 0.49	Cu 0.49	100.0
Pb 16.6	Pb 16.6	100.0
Hg 40.2	Hg 39.8	99.0
Cu 0.98	Cu 0.98	100.0
Pb 33.1	Pb 33.1	100.0
Hg 12.6	Hg 12.2	96.7
Cu 6.1	Cu 6.1	100.0
Pb 1.04	Pb 1.04	100.0
Hg 25.2	Hg 25.2	100.0
Cu 12.2	Cu 12.2	100.0
Pb 2.07	Pb 2.07	100.0
Hg 2.52	Hg 2.42	96.2
Cu 4.90	Cu 4.90	100.0
Pb 10.35	Pb 10.35	100.0
Hg 1.00	Hg 0.97	97.0
Cu 1.97	Cu 1.98	100.8
Pb 4.14	Pb 4.14	100.0

In these experiments the metals were added to the ammonium
acetate extracting solution in the form of standard solutions of their
nitrates, and the foregoing procedure was then applied. The precision
of the measurements was about ± 2%, and it appeared to be limited only
by the accuracy of measuring the wave heights. Fig. 2 is a repre-
sentative polarogram obtained by this procedure, in which wave a is
due to mercury (0.101 millimolar), wave b due to copper (0.077 milli-
molar), and wave c due to lead (0.080 millimolar).

Detailed Method of Analysis

To the primer sample, which may contain mercuric fulminate, lead
azide, cuprous thiocyanate, stibnite, and potassium chlorate or nitrate,
is added 40 cc. of 2 M ammonium ac ate and 2 cc. of 30% hydrogen
peroxide. The solution is warmed under reflux on the steam bath until
complete solution of all but the stibnite has taken place. The residue
of stibnite is collected on a filter and washed with 10 cc. of the
original ammonium acetate solution. The extract and the washings are
combined in a 125-cc. Erlenmeyer flask. To this solution is added
2.00 g. of 20-mesh zinc of the highest purity on which a blank has
previously been run. The flask is then fitted with a small paddle
stirrer and stirred for two hours at such a rate that the major portion
of the zinc is mildly tumbled at all times. It is advisable to add the
zinc in two portions, a gram at a time, about an hour apart. This is
due to the fact that as the copper plates out it slows the removal of
the mercury. By adding the zinc in two portions the copper is largely
removed on the first portion, leaving the fresh surface of the second
for the removal of the mercury. At the end of the plating period the
metal is collected, and to it are added 11 cc. of concentrated nitric
acid (dropwise, and with cooling), the calculated quantity to dissolve
the zinc and give a final concentration of 1 M free nitric acid. The
solution is quantitatively transferred to a 100-cc. volumetric flask,
1 cc. of 1% gelatin added, and the solution brought to volume. It is
then polarographed, using a saturated mercurous sulfate electrode in
the H-cell of Lingane and Laitinen.[5] From the measured diffusion

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(5) J. J. Lingane and H. A. Laitinen, Ind. Eng. Chem., Anal. Ed.,
11, 504 (1939).
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current,[3] drop-time, and m-value the concentrations are calculable.[3]

The stibnite residue is plac in the flask of the sulfide still
with 10 cc. of alkaline tartrate solution (2 M potassium tartrate +
1 M KOH). To the main receiver is added 5.0 g. of reagent quality
potassium iodide and a sufficient volume of standard potassium iodate
to leave an excess of about 20% above that required by the expected
amount of hydrogen sulfide. Then 5 cc. of 0.2 M potassium hydroxide
is placed in the test-tube, the joints are lightly lubricated with
petroleum jelly, and the apparatus is assembled. A slow current of

nitrogen is bubbled through the sy.tem for ten minutes to sweep out the air, and then a small flame from a micro burner is applied to the still flask. The solution is brought to the boiling point and held there until solution of the stibnite has taken place, usually about thirty minutes. After boiling for fifteen minutes of this time, the receiving bottle is slipped below the bubbler tube, 15 cc. of 1 M hydrochloric acid is added, and the bottle quickly replaced. Ten cc. of concentrated hydrochloric acid is then added tn the still reservoir, a quantity sufficient to make the contents of the still 4-5 M in free acid, and to make the solution, upon dilution to 100 cc., 1 M in free acid.

When solution is complete the flame is removed, the flask allowed to cool slightly, and the nitrogen stream adjusted so that bubbles still issue slowly and regularly from the absorption system. The concentrated acid is added to the still flask through the stopcock, the flame again applied, the nitrogen stream readjusted, and the distillation allowed to proceed for one hour. At the end of the distillation the bubbler is slipped from the rubber connection, the contents of the test-tube added to the main receiver, and the bubbler and test-tube are washed into the main receiver. The whole solution is immediately titrated with standard sodium thiosulfate, using starch as an indicator in the usual manner.

The solution in the still flask is transferred, with the washings from the inner tube of the condenser, to a 100-cc. volumetric flask, 1 cc. of 1% gelatin solution is added, and the solution is brought to volume. The antimony wave is then recorded in the same manner as the other metals, and the same techniq. applied to determine the concentration.

Discussion of Results

Table VIII contains data on the complete analysis according to the methods herein outlined. It can be seen that the recovery of mercury is the poorest of any of the metals involved. The presence of thiocyanate ion or its oxidation products does not seem to affect the recovery of lead, which is approximately the same in the cases where thiocyanate ion is or is not present.

The sulfide determination is subject to errors already pointed out, the possible oxidation by ferric iron, and incomplete absorption by the iodine (we found it practically impossible to obtain complete absorption of the gas in any medium used). Therefore the antimony would be a more reliable guide to the stibnite content.

Table VIII
Analysis of Synthetic Primer Mixtures

Sample No.	Wt. sample, mg.				% Recovery				
	$Hg(OCN)_2$	CuCNS	$PbOHN_3$	Sb_2S_3	Hg	Cu	Pb	Sb	S
1	33.6	18.8	27.0	16.0	46.2	97.4	95.0	96.2	90.4
2	25.9	5.9	29.0	17.5	53.3	78.2	93.5	100.0	95.5
3	26.5	11.6	37.8	18.0	96.3	93.5	94.8	98.7	98.5
4	26.0	9.7	37.0	18.0	98.2	96.7	93.0	96.2	97.8
5	29.0	5.9	16.9	17.4	100.0	96.6	99.1	86.2	84.5
6	13.9	6.8	13.2	7.5	99.0	106.0	90.0	92.5	56.2
7	50.8		50.5	50.3	95.0		98.1	99.0	87.4
8	102.3		100.3	100.2	99.4		97.6	94.4	86.6
9	24.3		28.7	28.4	91.8		95.3	96.8	94.0
10	24.3		24.1	21.2	95.0		92.9	96.7	93.9
11	15.8		15.1	18.?	69.4		76.6	98.0	92.0
12	16.8		16.7	17.?	98.4		98.0	97.5	92.0

(potassium chlorate was present in all samples in
the same order of weight as the other components)

We have determined that the plating process is completely
efficient, so that the observed errors cannot be due to this stop. A
possible source of error is incomplete extraction of the components
by the ammonium acetate. If this is the case, part of the "soluble"
material will remain with the stibnite residue, and can then be found
with the antimony. When this happens the final concentration of metal
can be regarded as the sum of the concentrations obtained from the
plated zinc and that found with the antimony residue.

We feel that in addition to furnishing a roughly quantitative
voltammetric analysis for the azide ion, we have developed a quantitative
polarographic method for the analysis of simple primer mixtures, which
can be extended to include other components, and which can doubtless be
improved by further experimentation.

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ABSTRACT: *Unclass*
   The report describes a technique whereby very small amounts of mixtures of inorganic compounds, commonly found in primers and detonators, can be analyzed quantitatively by means of the polarograph. Investigations were confined to a typical mixture composed of potassium chlorate, cuprous thiocyanate, antimonous sulfide (stibnite), lead azide, and mercury fulminate. The mercuric fulminate was analyzed by dissolving a weighed sample in 2 M ammonium acetate in the steam bath, diluting it to a known volume, and recording the polarograph. The stibnite was analyzed by dissolving it in concentrated hydrochloric acid, boiling to remove hydrogen sulfide, dilution to a volume of 100 cc, which was 1 M in free hydrochloric acid, and recording the polarograph. Analysis of the lead azide for lead content was made in the same manner as that for mercury in mercuric fulminates. The azide ion was determined cerimetrically.

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