Electric Spark Sensitivity of Reductive Element–Oxidizer Mixtures

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ABSTRACT

Electric spark sensitivities were determined for mixtures of a reductive element and an oxidizer using three types of testers. One tester is a simplified electric spark tester which distinguishes high-sensitivity energetic materials from medium- or low-sensitivity materials. The other two testers determine the 50% ignition energies; one, for high-sensitivity materials, and the other for medium-sensitivity materials.

Typically the reductive elements give the following order of decreasing sensitivity when mixed with oxidizers: Zr > P > B > Al > Mg > S > Si. Without any other oxidizer present, Zr and P are high-sensitivity materials in air. The other elements do not ignite without oxidizer present in the apparatus used. The results from the simplified tester agree with results from the tester for high-sensitivity materials; however, some do not agree with those obtained from the tester for medium-sensitivity materials. This is partly attributed to the difference in the way the samples are confined in the apparatus. Correlations were also examined between the results of the electric spark tester and results from both the drop ball test and the friction test.

Keywords: reductive element, fuel, oxidizer, electric spark sensitivity

1. Introduction

In fireworks, mixtures of a reductive element and an oxidizer have been used for producing pyrotechnic effects such as light, color, smoke and propulsion.[1] Mixtures of reductive elements and oxidizers are sometimes highly sensitive to impact, friction, heat or electric spark.

One of the authors of this paper has previously developed two electric spark testers, one for medium-sensitivity and the other for high-sensitivity energetic materials.[2] The two testers have been used for evaluating the electric spark sensitivities of primary explosives, secondary high explosives, pyrotechnic compositions and mixtures of oxidizers and combustible materials.[3] Recently, Hosoya Kako Company developed a new simplified electric spark tester[4]

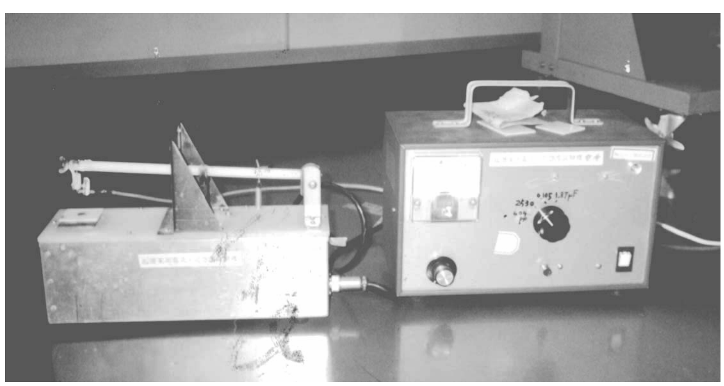

Photo 1. The tester for high-sensitivity materials.

Photo 2. The tester for medium-sensitivity materials.

intended for use by manufacturers of fireworks to assess the safety of materials.

We have collected data on the electric spark sensitivity of mixtures of reductive elements and oxidizers using the three tests mentioned above and have examined the relationships between the results from the different testers. We have also examined the correlations between the BAM friction sensitivities and the electric spark sensitivities of the mixtures determined with the drop ball. Herein we describe the results of our experiments on the electric spark sensitivity of mixtures of reductive elements and oxidizers.

2. Experimental

2.1 Materials

The reductive elements examined are red phosphorus (P), zirconium (Zr), sulfur (S), magnesium (Mg), aluminum (Al), silicon (Si), and boron (B).

The oxidizers studied are potassium perchlorate ($KClO_4$), potassium chlorate ($KClO_3$), potassium nitrate (KNO_3), barium nitrate ($Ba(NO_3)_2$), strontium nitrate ($Sr(NO_3)_2$), copper(II) oxide (CuO), lead(II) nitrate ($Pb(NO_3)_2$), lead(IV) oxide (PbO_2), red lead (Pb_3O_4), iron(III) oxide (Fe_2O_3), calcium peroxide (CaO_2) and barium peroxide (BaO_2). All of the samples are in the form of powder; the elements and oxidizer are manually mixed together on parchment.

2.2 Apparatus

The three testers are shown in Photos 1–3, their electric circuits are shown in Figures 1–3, and the electrode discharge assemblies are shown in Figures 4–6. The simplified tester is used for distinguishing high-sensitivity materials from the medium- and low-sensitivity materials. This tester has fixed output energy (ca. 50 mJ), fixed

Photo 3. The simplified tester.

bar-plate electrodes, and an open sample holder. The distance between the electrodes is 2 mm. The amount of sample is approximately 5 mg, which is determined by considering the violence of the reaction. This tester can also be used to screen materials before the other two testers are used.

The tester for high-sensitivity materials is used for evaluating the sensitivities of primary explosives, igniter compositions, and highly sensitive pyrotechnic compositions. The tester has variable capacitance energies (8.0×10^{-6} to 8.0×10^{-1} J), movable needle–plate electrodes, and holds approximately 10 mg of sample in an open well.

The tester for medium-sensitivity materials is used for secondary explosives, propellants, gas generators, intermediately sensitive pyrotechnic compositions, and self-reductive chemicals. The tester has large capacitance energies (1.0×10^{-2} – 82 J), confined fixed-bar electrodes, and can hold a 30 mg sample in a sealed PVC tube. The outside diameter of the tube is 5 mm, and the distance between the electrodes is fixed at 1.5 mm.

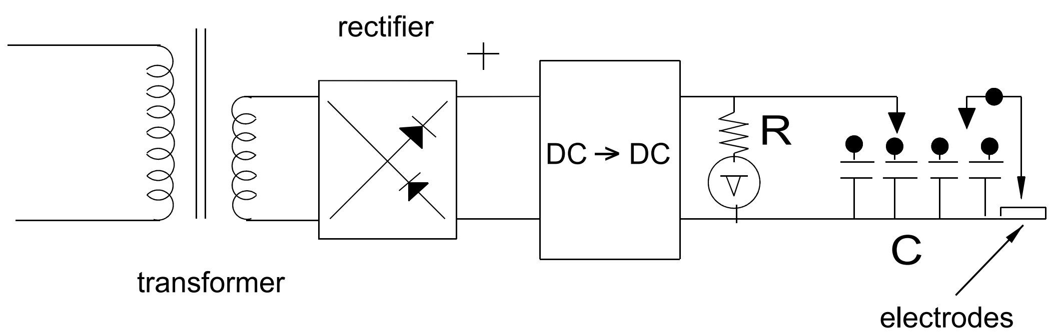

Figure 1. The electric circuit of the tester for high-sensitivity materials.

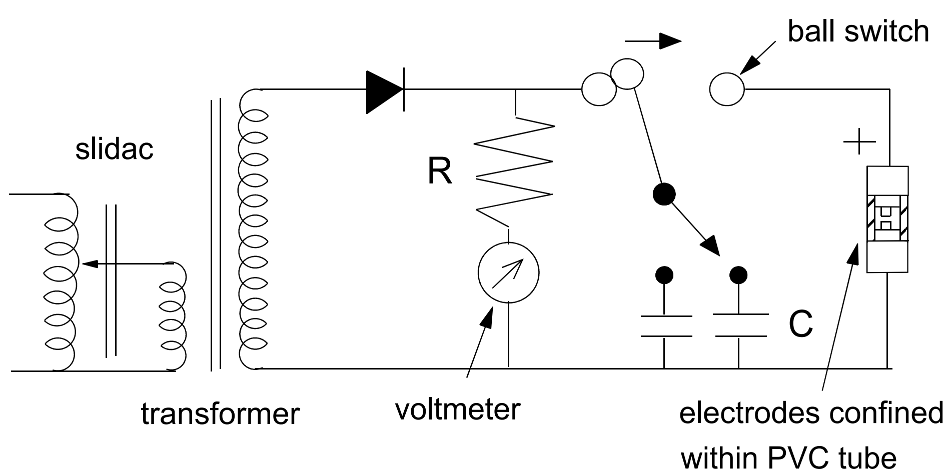

Figure 2. The electric circuit of the tester for medium-sensitivity materials.

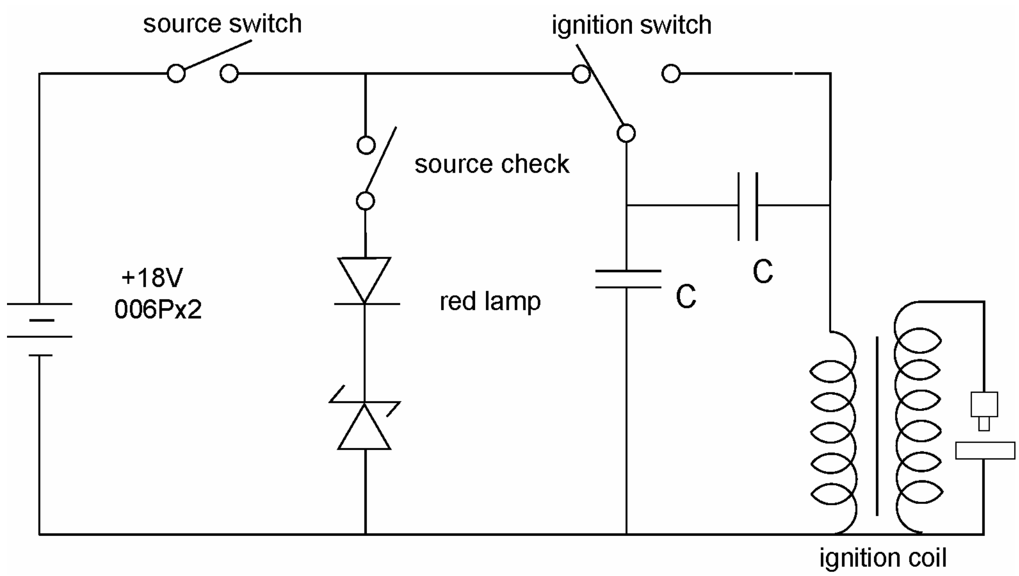

Figure 3. The electric circuit of the simplified tester.

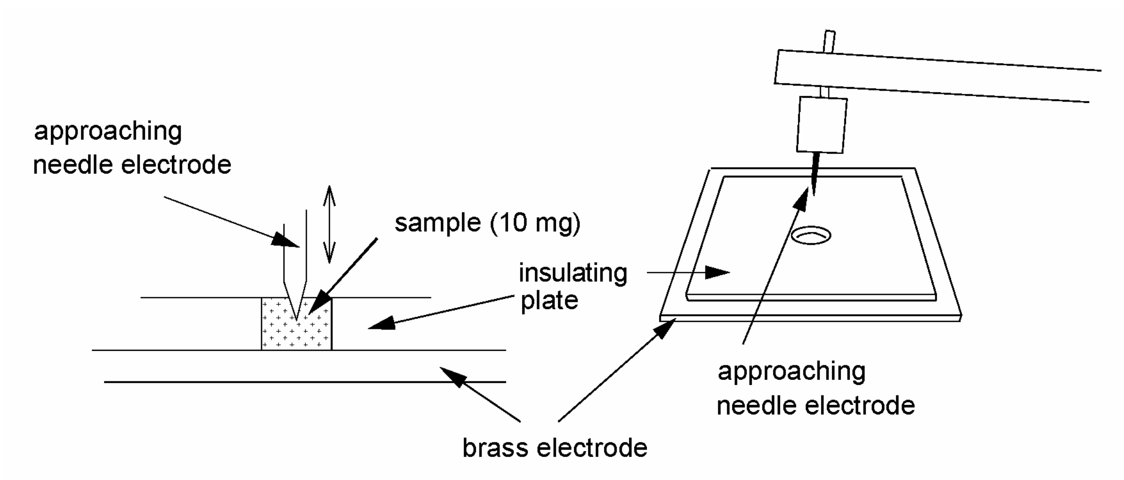

Figure 4. The discharge electrode assembly of the tester for high-sensitivity.

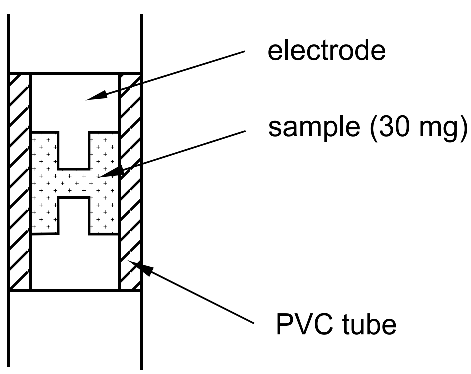

Figure 5. The discharge electrode assembly of the tester for medium-sensitivity.

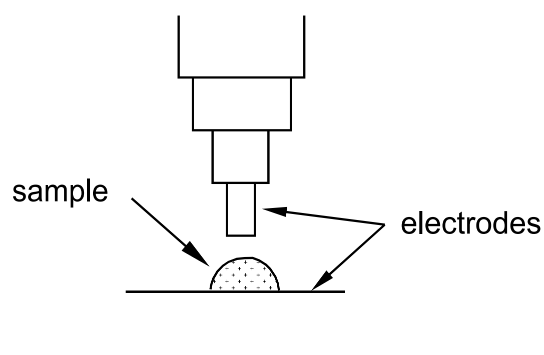

Figure 6. The discharge electrode assembly of the simplified tester.

2.3 Procedure

2.3.1 The Simplified Tester

(1) Put about 5 mg of sample on the lower electrode plate.

(2) Set the upper electrode bar above the sample.

(3) Switch on the power source.

(4) Push the check button to confirm the source voltage.

(5) After the count down, push the ignition button to discharge the electrodes.

(6) Repeat the trial 10 times on a different area of the lower electrode plate.

(7) After 10 trials, clean both electrodes with sandpaper.

(8) Noise, flame and smoke are judged as positive results.

(9) Results are expressed as the number of positive results ("○" in tables; "go" on graphs) out of 10 trials; (negative results are "×" or "no go").

(10) Qualitative assessment of the relative violence of a reaction in this test is also valuable information.

2.3.2 The Tester for High-Sensitivity Materials

(1) Weigh 10 mg of sample and put it in the hole of the lower electrode.

(2) Switch on the power source.

(3) Set the capacitance dial to an appropriate capacitance.

(4) Set the voltage dial to an appropriate voltage.

(5) Push the ignition button.

(6) Ignition occurs if explosion, combustion or smoke is visible.

(7) Repeat the test 20 times according to Bruceton's up-and-down method.

(8) Confirm the voltage decreased to zero.

(9) Clean the electrodes with sandpaper and cloth after every run.

(10) Treat the resultant data by Bruceton's method.

2.3.3 The Tester for Medium-Sensitive Materials

(1) Select appropriate condensers and connect them.

(2) Put 30 mg of sample into the PVC tube set on the lower electrode.

(3) Switch on the power source.

(4) Adjust the voltage to the appropriate level using the voltage dial.

(5) Push the ignition button to discharge a spark at the sample.

(6) Ignition is judged to occur if the PVC tube ruptures, if noise is heard, or if the sample disappears.

(7) Conduct 20 trials according to Bruceton's method.

(8) Allow the discharge bar to contact the ball switch to discharge any residual electricity.

(9) Clean the electrodes with sandpaper and tissue paper after every trial.

(10) Treat the resultant data by Bruceton's method.

3. Results

3.1 The Simplified Tester

Examples of the treatment of data from the simplified tester are shown in Table 1. The final results from the tester are listed in Table 2. The E_{50} value is the 50% ignition energy determined by the testers for high- and medium-sensitivity materials.

Table 1. Examples of the Treatment of the Data by the Simplified Tester.

Sample	Run 1	2	3	4	5	6	7	8	9	10	Ignition /10	Observation
$P/KClO_4$	○	○	○	○	○	○	○	○	○	○	10/10	Explosion
$Al/KClO_4$	○	○	×	○	×	○	○	×	○	○	7/10	Flash
S/KNO_3	×	×	×	×	×	×	×	×	×	×	0/10	No reaction

Table 2. Results from the Simplified Tester and E_{50} Values from the Other Testers.

Sample	Ignition /10	Observation	Sensitivity	E_{50} (J)	Type of Tester
Zr	10/10	combustion	high	7.6×10^{-5}	High
$Zr/KClO_4$	10/10	flash, smoke	high	2.6×10^{-4}	High
Zr/CaO_2	0/10		not high	3.2×10^{-1}	Medium
Si	0/10		not high	82<	Medium
Si/BaO_2	0/10		not high	2.1×10^{-1}	Medium
Si/CaO_2	0/10		not high	29	Medium
B	0/10		not high	82<	Medium
B/KNO_3	0/10		not high	1.1	Medium
$B/Pb(NO_3)_2$	0/10		not high	4.9×10^{-2}	Medium
B/CaO_2	0/10		not high	3.8	Medium
$B/KClO_3$	0/10		not high	3.7×10^{-2}	Medium
S	0/10		not high	82<	Medium
S/BaO_2	0/10		not high	9.3×10^{-1}	Medium
$S/Ba(NO_3)_2$	0/10		not high	9	Medium
$S/KClO_3$	0/10		not high	1.4	Medium
Mg	0/10		not high	82<	Medium
$Mg/KClO_4$	0/10		not high	6.4×10^{-1}	Medium
Mg/CaO_2	0/10		not high	1.4	Medium
Mg/CuO	0/10		not high	8.3×10^{-1}	Medium
Al	0/10		not high	82<	Medium
$Al/KClO_4$	7/10	flash, smoke	high	1.8×10^{-1}	Medium
Al/BaO_2	1/10	fire	high	1.9×10^{-2}	High
$Al/Ba(NO_3)_2$	0/10		not high	7.4×10^{-1}	Medium
Al/CaO_2	0/10		not high	1.2×10^{-1}	Medium
$Al/KClO_3$	2/10	flash	high	4.9×10^{-1}	High
P	10/10	combustion, smoke	high	5.6×10^{-3}	High
$P/KClO_4$	10/10	fire, smoke	high	2.7×10^{-2}	High
P/KNO_3	10/10	fire, smoke	high	2.8×10^{-2}	High
P/BaO_2	10/10	fire, smoke, flash	high	2.9×10^{-1}	High
$P/Ba(NO_3)_2$	10/10	flash, fire	high	5.6×10^{-1}	High
$P/Pb(NO_3)_2$	8/10	fire, smoke	high	2.5×10^{-2}	High
P/CaO_2	10/10	flash	high	2.2×10^{-1}	High
$P/KClO_3$	10/10	sound, fire, smoke	high	9.1×10^{-3}	High
P/CuO	10/10	fire, smoke	high	7.8×10^{-3}	High
P/Pb_3O_4	10/10	fire, smoke	high	2.6×10^{-2}	High
P/PbO_2	10/10	fire, smoke	high	1.8×10^{-2}	High

* Columns headed Ignition, Observation and Sensitivity show results from the simplified tester.

** Columns headed E_{50}(J) and Type of Tester list results from the other two testers.

3.2 Testers for High- and Medium-Sensitivity Materials

The data from both of these testers is treated in the same fashion. An example is shown in Table 3. Figure 7 shows a plot of the sensitivities of the reductive element and the element–oxidizer mixtures determined by the two testers.

Table 3. An Example of Data Treatment for Red Phosphorus.

Sample:	red phosphorus	Capacitance:	0.098 µF
Mass:	5 mg	Increment of logV:	0.1
Tester:	high-sensitivity	Observation:	combustion

Data from the up-and-down method: 20 trials (O = go × = no go)

logV		O	×
2.75	O	1	0
2.65	O O × ×	3	1
2.55	O O O × × O ×	4	3
2.45	O O × × × ×	2	4
2.35	× ×	0	2
		10	10

Data treatment

logV	V(v)	E(J)	n(O)	i	i · n	$i^2 \cdot n$
2.75	560	0.015	1	0	0	0
2.65	450	0.010	3	1	3	3
2.55	355	0.006	4	2	8	16
2.45	280	0.004	2	3	6	18
2.35	220	0.002	0	4	0	0
			Ns=10		A=7	B=37

Results

$\log V_{50} = 2.53$

$V_{50} = 338.8$ (V)

$\sigma v = 0.14$

$\log E_{50} = -2.25$

$E_{50} = 0.0056$ (J)

$\sigma_E = 0.27$

Table 4. List of the Electric Spark Sensitivities Determined with Testers for High-and Medium-Sensitivity Materials.

Sample	Tester	Mass (mg)	$LogE_{50}$	σ_E
P	High	3	–2.25	0.27
$P/KClO_4$	High	3	–1.57	0.08
P/KNO_3	High	3	–1.55	0.06
P/BaO_2	High	3	–0.54	0.44
$P/Ba(NO_3)_2$	High	3	–0.26	0.07
$P/Pb(NO_3)_2$	High	3	–0.61	0.16
P/CaO_2	High	3	–0.66	0.43
$P/KClO_3$	High	3	–2.04	0.15
P/CuO	High	3	–2.11	0.15
P/Pb_3O_4	High	3	–1.59	0.09
P/PbO_2	High	3	–1.75	0.43
Zr	High	10	–4.12	0.23
$Zr/KClO_4$	High	10	–3.58	0.1
Zr/KNO_3	High	10	–3.79	0.08
Zr/BaO_2	High	5	–4.26	0.35
$Zr/Ba(NO_3)_2$	High	5	–2.54	0.23
$Zr/Pb(NO_3)_2$	High	5	–3.42	0.22
Zr/CaO_2	Medium	5	–0.49	0.14
$Zr/KClO_3$	High	5	–1.96	0.33
Zr/CuO	High	5	–3.88	0.06
Zr/Pb_3O_4	High	5	–4.62	0.35
Zr/PbO_2	High	5	–3.84	0.14
B	Medium	30	>1.9	—
$B/KClO_4$	Medium	30	–1.3	0.08
B/KNO_3	Medium	30	0.06	0.19
B/BaO_2	High	5	–2.48	0.37
$B/Ba(NO_3)_2$	Medium	30	1.42	0.18
$B/Pb(NO_3)_2$	Medium	30	–1.31	0.19
B/CaO_2	Medium	30	0.58	0.18
$B/KClO_3$	Medium	30	–1.43	0.15
B/CuO	High	5	–1.59	0.09
B/Pb_3O_4	Medium	30	1.33	0.15
B/PbO_2	High	5	–3.62	0.15
Al	Medium	30	>1.9	—
$Al/KClO_4$	Medium	10	–0.76	0.15
Al/KNO_3	Medium	10	0.25	0.16
Al/BaO_2	High	3	–1.73	0.11
$Al/Ba(NO_3)_2$	Medium	30	–0.13	0.21
$Al/Pb(NO_3)_2$	Medium	30	1.28	0.3

Table 4. List of the Electric Spark Sensitivities Determined with Testers for High-and Medium-Sensitivity Materials. (Continued)

Sample	Tester	Mass (mg)	$LogE_{50}$	σ_E
Al/CaO_2	Medium	10	–0.93	0.33
$Al/KClO_3$	High	5	–0.31	0.16
Al/CuO	Medium	10	–0.83	0.18
Al/Pb_3O_4	Medium	20	–0.31	0.15
Al/PbO_2	Medium	20	–0.81	0.15
Mg	Medium	30	>1.9	—
$Mg/KClO_4$	Medium	10	–0.19	0.04
Mg/KNO_3	Medium	10	0.67	0.14
Mg/BaO_2	Medium	20	0.97	0.3
$Mg/Ba(NO_3)_2$	Medium	20	0.57	0.28
$Mg/Pb(NO_3)_2$	Medium	30	0.39	0.16
Mg/CaO_2	Medium	30	0.15	0.08
$Mg/KClO_3$	Medium	30	–1.37	0.16
Mg/CuO	Medium	30	–0.08	0.23
Mg/Pb_3O_4	Medium	30	1.68	0.08
Mg/PbO_2	Medium	30	–0.08	0.27
Si	Medium	30	>1.9	—
$Si/KClO_4$	Medium	30	1.14	0.14
Si/KNO_3	Medium	30	1.05	0.07
Si/BaO_2	Medium	30	–0.68	0.3
$Si/Ba(NO_3)_2$	Medium	30	1.25	0.15
$Si/Pb(NO_3)_2$	Medium	30	1.72	0.09
Si/CaO_2	Medium	30	1.46	0.14
$Si/KClO_3$	Medium	30	1.36	0.27
Si/CuO	Medium	30	1.58	0.33
Si/Pb_3O_4	Medium	30	>1.9	—
Si/PbO_2	Medium	30	1.9	—
S	Medium	30	>1.9	—
$S/KClO_4$	Medium	30	1.26	0.29
S/KNO_3	Medium	30	1.24	0.08
S/BaO_2	Medium	30	–0.03	0.14
$S/Ba(NO_3)_2$	Medium	30	0.95	0.22
$S/Pb(NO_3)_2$	Medium	30	1.09	0.08
S/CaO_2	Medium	30	1.07	0.31
$S/KClO_3$	Medium	30	0.15	0.15
S/CuO	Medium	30	1.69	0.09
S/Pb_3O_4	Medium	30	1.67	0.08
S/PbO_2	Medium	30	1.54	0.22

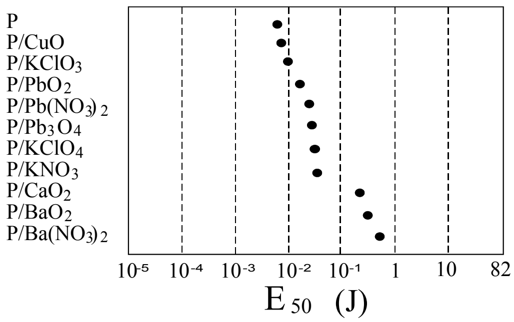

Figure 7(A). Plot of sensitivities of red phosphorus and red phosphorus–oxidizer mixtures.

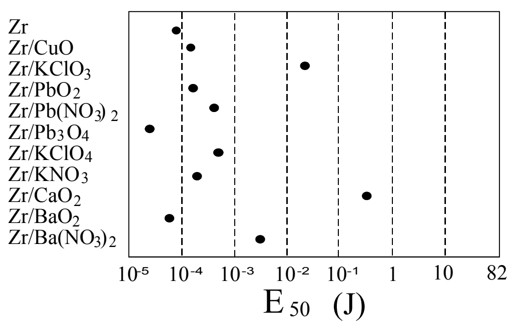

Figure 7(B). Plot of sensitivities of zirconium and zirconium–oxidizer mixtures.

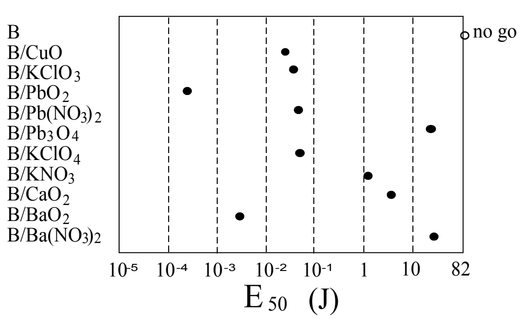

Figure 7(C). Plot of sensitivities of boron and boron–oxidizer mixtures.

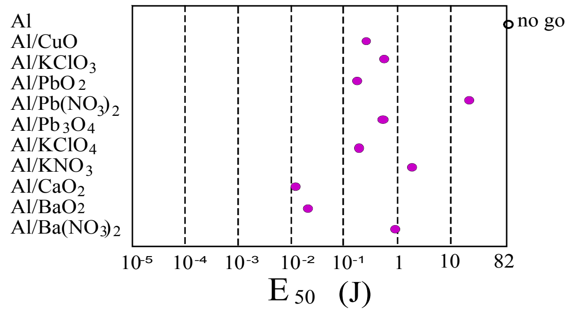

Figure 7(D). Plot of sensitivities of aluminum and aluminum–oxidizer mixtures.

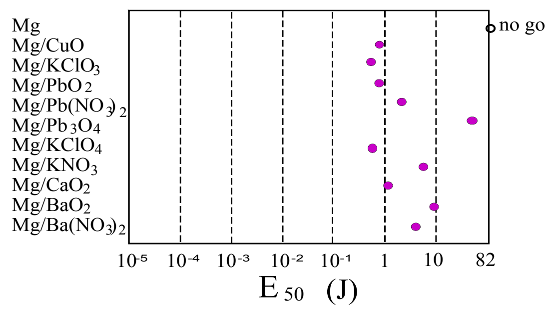

Figure 7(E). Plot of sensitivities of magnesium and magnesium–oxidizer mixtures.

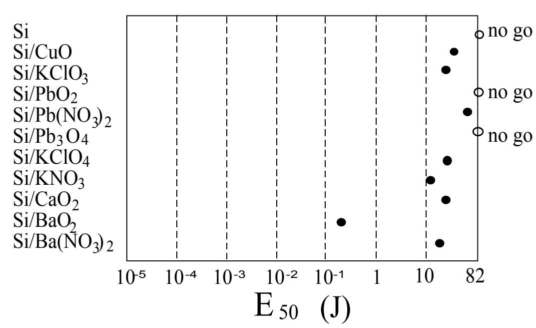

Figure 7(F). Plot of sensitivities of silicon and silicon–oxidizer mixtures.

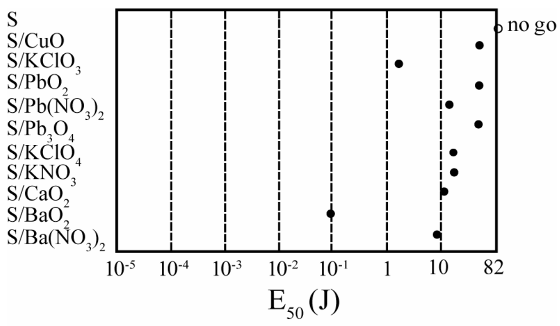

Figure 7(G). Plot of sensitivities of sulfur and sulfur–oxidizer mixtures.

4. Discussion

4.1 Electric Spark Sensitivities of the Reductive Elements Alone

Only zirconium and red phosphorus powders ignite in the tester for high–sensitivity materials in the absence of added oxidizer. The other reductive elements (Al, B, Mg, Si and S) were not ignited in air at room temperature by an 82 J electric spark in the tester for medium–sensitivity materials.

The spark sensitivity of red phosphorus decreases when the element is mixed with any of the oxidizers, which suggests the oxidizers act as inert diluents for red phosphorus. In the case of Zr, only Pb_3O_4 and BaO_2 activate it for ignition; the other oxidizers deactivate Zr. The other reductive elements are all activated when mixed with the oxidizers.

4.2 Electric Spark Sensitivities of Element–Oxidizer Mixtures by the Two Conventional Testers

Among the mixtures examined, most Zr mixtures show the highest sensitivities. Therefore, the Zr–$KClO_4$ composition with a value of logE_{50} = –3.6 is used as an igniter instead of tricinate, the E_{50} value of which is –4.4 in the same tester.

The sensitivities of the red phosphorus–oxidizer mixtures are the next highest. The range of sensitivities of these mixtures is rather small: from 0.01 to 1.0 J. In these mixtures, CaO_2, BaO_2, and $Ba(NO_3)_2$ seem to act as ignition retardants.

In all the mixtures of elements other than Zr and P, oxidizers act as promoters for the spark ignition of the elements. BaO_2 is the most effective for increasing the sensitivities of many elements but was ineffective for Mg. The most effective oxidizer for increasing the sensitivity of Mg was $KClO_3$.

Among Al, B, Mg, S and Si mixtures with the oxidizers, B gave the highest sensitivity with BaO_2, then Al with BaO_2, Mg with $KClO_3$, Si with BaO_2, and S with BaO_2. On the average, the order of decreasing sensitivity of these elements when mixed with oxidizers is: Zr > P > B > Al > Mg > S > Si.

4.3 Deviation in Test Results

The average standard deviations (σ) in the values of log E_{50} from the electric spark tests are 0.18 for medium–sensitivity materials and 0.20 for high–sensitivity materials. These deviations are similar to those found in the visual small gap test, the shock ignitability test, the small drop ball test, the drop hammer test, and the BAM friction test.[6–8]

4.4 Comparison of the Results of the Simplified Tester and the Two Conventional Testers

Data from the three testers are plotted in Figure 8.

The materials identified as high–sensitivity by the tester for high–sensitivity were also all identified as high–sensitivity materials by the simplified tester. Most of the materials classified as not highly sensitive by the simplified tester were placed in the medium–sensitivity category by the tester for medium–sensitivity materials.

The output energy of the simplified tester is fixed at ca. 50 mJ. The correlations shown in Figure 8 are reasonable.

However some mixtures do not ignite in the simplified tester even though they have an E_{50} value lower than 0.8 J as determined in the tester for medium–sensitivity materials. It has recently been shown that the values of E_{50} measured by the tester for high–sensitivity materials are larger than those measured by the tester for medium–sensitivity materials as listed in Table 5.[3]

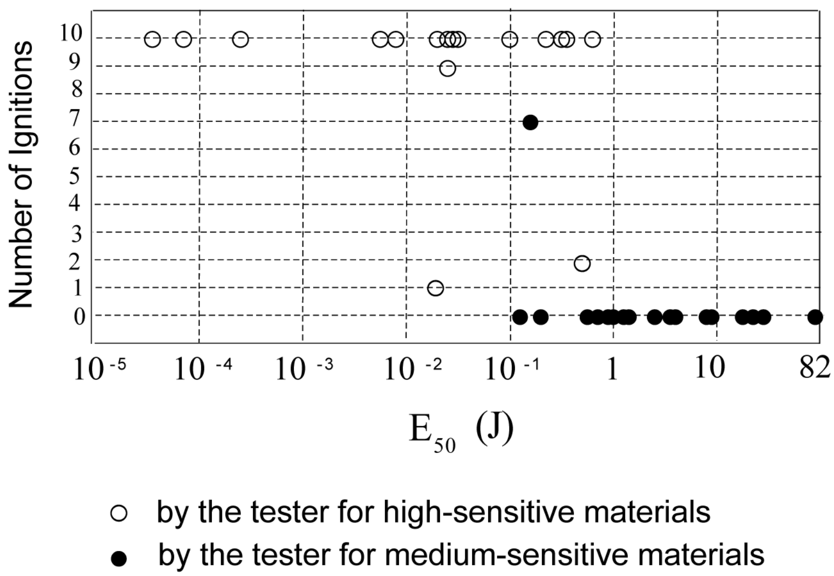

Figure 8. Plot of the number of ignitions in the simplified tester against E_{50} from the two conventional testers.

Table 5. Comparison of Values of E_{50} as Measured by Two Testers.

Materials	Log E_{50} high	Log E_{50} medium	Difference
$Pb(N_3)_2$/dextrin	–0.95	–1.64	0.96
tetrazene/starch(50/50)	–0.65	–1.75	1.07

The difference in the results from the two testers may be partly explained by the different ways the sample is contained. The sample in the simplified tester is put on a plate, and the sample in the high–sensitivity tester is placed in an open well. Part of the discharge energy escapes into the surroundings. Therefore the efficiency of the spark discharge in the two testers may be lower than in the tester for medium–sensitivity materials, in which the sample is confined in a PVC tube with the upper and lower electrodes inserted in it. The confinement may also accelerate the rise in pressure, the accumulation of heat, and the ignition of the sample.

4.5 Correlations of Electric Spark Sensitivities with Impact and Friction Sensitivities

Among the different drop weight tests, the direct impact drop ball test gives the lowest E_{50} values for material with the same energy ratings. The correlation between the results of the electric spark test and the drop ball test is shown in Figure 9.[6] The values of E_{50} from the drop test and the spark test are similar for medium–sensitivity materials such as RDX, HMX and black powder, and also for some high–sensitivity materials such as red phosphorus–oxidizer mixtures. This indicates that the efficiency of the added energy is nearly the same for these materials in both tests. For high–sensitivity materials such as pure $Pb(N_3)_2$, trichinate and Zr–$KClO_4$, the energy efficiency is much lower for the drop ball test than for the spark test.

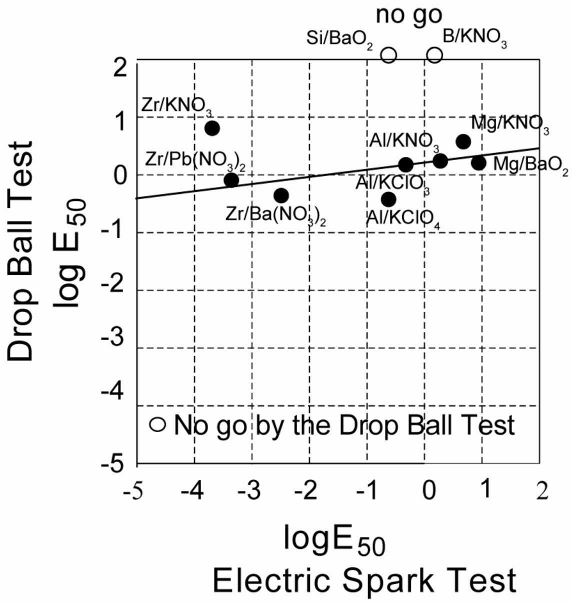

Figure 9. Correlation between values from the electric spark test and the direct drop ball test.

Correlation in the data from the electric spark test and the BAM friction test[7] are shown in Figure 10. The results are similar to those from drop ball and electric spark test.

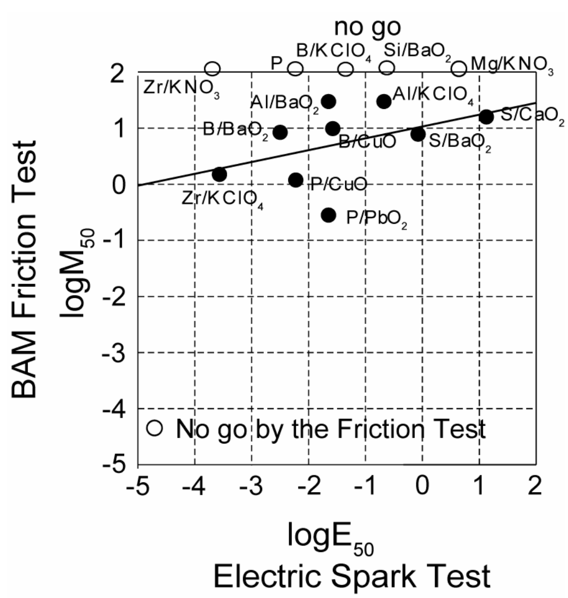

Figure 10. Correlation between values from the electric spark test and the friction test.

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