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TIME DEPENDENT ELECTRON PARAMAGNETIC RESONANCE CHARACTERISTICS OF DETONATED PRIMER RESIDUES

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PREFACE

Preliminary experiments in our laboratory suggested to us that electron paramagnetic resonance (EPR) spectrometry was, potentially, a powerful tool in a sharply defined area of forensic criminalistics. We demonstrated in these experiments that the pyrolysis of primer compounds and gunpowders which occurs upon the discharge of a cartridge imparts to these materials an EPR signal indicative of the presence of free radicals. These pyrolytically induced free radicals were, as would be expected, observed to disappear with time, as reflected in serial EPR spectra obtained from each residue over a period of time, in one case extending to 19 days after discharge of the cartridge case. Even though the number of samples was small, there was a strong indication that each of the materials examined possessed EPR decay curves that could be characteristic of the manufacture of that material. Thus, we felt there was the potential of defining with EPR spectrometry the following factors, given the appropriate physical evidence in a criminal case:

1) if a firearm or cartridge case had recently been discharged,
2) when that firearm or cartridge case was discharged,
3) the manufacture of cartridge employed in a recently discharged firearm.

On the bases of the results of these preliminary experiments, we sought from and were granted by LEAA a pilot project to further investigate the time dependent nature of the EPR signal of gunpowder and primer residues. A concatenation of factors determined for us that our pilot project would be limited to an investigation of primer residues. These factors included instrument sensitivity, mass of recoverable sample, and time-frame of the pilot project. The report that follows represents the results obtained from the post-detonation residues of five brands of primers obtained immediately after the discharge of fixed ammunition of each brand. Multiple samples were obtained from each brand.

The results from this pilot project tend to confirm our earlier studies and indicate to us that further study may establish the EPR spectrometer as a valuable tool in the armamentarium of the forensic criminalist.

SUMMARY

The purpose of this feasibility study was to determine if the time dependent EPR signal induced in primer compounds by detonation could be characterized to such an extent as to permit their utilization by criminalists to:

1) determine if a primer compound had been discharged recently,
2) estimate elapsed time from discharge of the primer compound,
3) establish manufacture of the primer compound.

Originally, as outlined in the grant proposal, the scope of the project was to include the examination of gunpowder as well as primer residues. As we got into the project, we realized that we would have to limit the scope of the project to either gunpowder or primer residues if we were to obtain an adequate number of samples from which we could obtain multiple spectra over elapsed time from discharge of the primer out to, in some instances, four weeks post-discharge. Accordingly, we examined residues from a total of 53 primers obtained from the discharge of five different brands of ammunition. From these samples, approximately 325 EPR spectra were obtained.

Primer residues were obtained from the inside surface of the primer cup as well as from the primer anvil and the cartridge case primer pocket of caliber .45 ACP fired ammunition (purchased through retail outlets) immediately after discharge of the cartridge. After the collection of a residue, it was weighed and then placed

into a fused quartz EPR sample holder in which it was stored throughout its analytical history. Presence of free radicals and their time-decay history was determined by EPR spectrometry for each individual sample. EPR spectra of the undetonated primer compounds served to establish that the spectra observed in the primer residues were induced by detonation and were not present in material not detonated.*

This feasibility study resulted in findings which indicated that each manufacture of primer possessed common EPR characteristics, i.e., there were easily discernible differences between brands of primers based on their EPR signal and the time-course decay of these signals. Sufficiently precise data were obtained on two of the five brands of primers to permit the determination of decay constants. Residues from the third brand of primer showed very low levels of EPR absorption and while the signal was observed to decay, the signal to noise ratio was so unfavorable that a reliable decay constant could not be determined from the data. Residues from the fourth brand of primer exhibited a very strong and very broad EPR signal which did not decay over the 20-day period these samples were analyzed. What appears to be a stable free radical was formed upon detonation of this brand of primer. The last brand of primer examined yielded interesting data in that this manufacturer purportedly does not manufacture

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* Undetonated primer was not obtained from Norma primers owing to the sealing technique employed in their manufacture.

his own primers, but purchases them for assembly into his brand of ammunition. Our data would indicate that either this manufacturer purchases his primers from more than one source or that he will accept primer compounds of varying compositions. In a series of ten samples, there were two distinct EPR signal morphologies. One sample exhibited a very strong EPR absorbance, while the remaining nine exhibited very similar and very weak EPR absorbances--too weak to be analyzed with existing equipment.

The problems experienced with those brands of primers which provided only a weak signal could, it is felt, be resolved, since with relatively minor instrument modification and some changes in sample handling technique, the signal:noise ratio could be substantially improved. Such improvement would likely permit the determination of a decay constant for the third brand of primer and possibly for those primers of the fifth brand which exhibited a very weak signal.

In brief, our findings are that under the conditions which this study was prosecuted, zero time data (t_0) can be extracted from the Peters and Remington military primer residues. With minor modifications to the instrumentation, zero time data could be extracted from the Western primer residues. All brands of primers studied yielded EPR signals distinct from each other and thus are classifiable as to manufacture.

We conclude that EPR spectrometry as employed in this feasibility study shows definite promise as a tool for forensic criminalistics. We have shown that under laboratory conditions, data are, within limits, reproducible and predictable. What remains to be shown are the following:

1) Can a relationship between mass of residue and strength of EPR signal be established?
2) Can residues be obtained from firearms which will permit similar conclusions to be drawn as from primer residues obtained from cartridge cases?
3) To what extent will different environments affect the induced EPR signal in primer residues and in gunpowder residues?
4) Given favorable outcomes to the above, then a systematic protocol for sample handling and analysis would be established that could be employed by crime laboratories adopting this technique.
5) Given favorable experimental results, a catalog of EPR spectra and EPR signal decay characteristics could be established according to manufacture of fixed ammunition and manufacture of reloading components.

These questions and procedures would constitute the basis of any subsequent study of the EPR characteristics of gunpowder and primer residues for which we may be funded.

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1. BACKGROUND

Among the chemical entities produced in the pyrolysis of gunpowders and their primers are free radicals.(1,2) These chemical entities are molecules or molecular fragments having unpaired electrons, a property which renders them paramagnetic. While stable free radicals do exist, most are chemically reactive and exist only as intermediates in chemical reactions. The disappearance of a given radical species through reaction with adjacent molecule(s) follows the usual laws of chemical kinetics. If the decay process is kinetically simple, it is possible that the time elapsed from the initiation of the reaction to a point on the decay curve (Δt) can be obtained.

This document reports the results of a pilot project undertaken by EG&G, Inc., to study the feasibility of using the time dependence of the free radical concentration in primer residues to determine the time of firing.

2. EXPERIMENTAL PROCEDURES AND MATERIALS

2.1 Primers

The primers chosen for examination in this study were all purchased through normal retail outlets, and are representative of those most commonly used. They were in all instances purchased as part of fixed ammunition in the .45 ACP caliber. Those chosen for study are listed in Table 1.

The ammunition was in all instances fired from a Colt 45 automatic pistol having a 4½ inch barrel. Immediately after firing the primer was removed from the spent case and primer residue obtained from the surfaces of the primer pocket of the cartridge case, the primer anvil and the primer cup. The residue was weighed to the nearest 0.1 mg (Table 2) and placed in a 8 mm ID x 15 cm long fused quartz tube.* The residue-containing tube was then stored in air at 23° C. A total of 53 primer residues were so processed prior to spectrometric examination.

The free radical concentration in each sample was measured by means of an Electron Paramagnetic Resonance (EPR) spectrometer. The time history of the free radical concentration was obtained through serial measurements of the individual samples, and extended up to four weeks. Each sample was composed of the residue extracted from a <u>single</u> primer and represented, therefore, a <u>minimum</u> sample quantity.

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* Purchased from Thermal American Fused Quartz Company, Montville, New Jersey.

Undetonated primer compounds from each brand of ammunition, except Norma, were examined for the presence of EPR signals. The resultant spectra were used to verify that those EPR signals detected in the detonated primer residues were not signals preexisting in the undetonated material. The undetonated Norma primer compound was not examined since the primer pellet was a solid mass cemented to the primer cup. Under the conditions which undetonated primer compound was removed from the primer cup in this study, it was felt that it was unsafe to attempt to remove the Norma primer pellet from its cup.

TABLE 1

PRIMER MANUFACTURERS

Brand	Lot No.	Manufacturer and Address
Peters	*	Peters Cartridge Division Remington Arms Company, Inc. Bridgeport, Connecticut
Super Vel	AG 211 2	Super Vel Cartridge Corp. Shelbyville, Indiana
Norma	09102	Norma Projektilfabrik Amotfors, Sweden
Western	82EF91	Olin Corp. Winchester-Western Division New Haven, Connecticut
Remington	RA 33092 (Military)	Remington Arms Co., Inc. Bridgeport, Connecticut

* Lot number not available.

TABLE 2

PRIMER RESIDUE WEIGHTS

Brand	Wt. (mg)	Sample Size
Peters	4.3 ± 0.8*	17
Super Vel	4.7 ± 0.4	10
Norma	4.9 ± 0.9	6
Western	3.1 ± 0.6	8
Remington (Military)	4.6 ± 0.3	6

* ± one standard deviation of the mean.

2.2 Instrumentation

All EPR measurements were made with a Varian E-4 spectrometer. The spectrometer was equipped with a rectangular TE_{102} cavity having a teflon positioning plug mounted through the cavity floor. This feature permitted the residue containing tubes to be reproducibly positioned in the cavity. In addition, the tubes were indexed so that their orientation with respect to the r-f magnetic field could be maintained.

Variations in the signal amplitude from the samples due to changes in cavity Q ($Q = 2\pi$ energy stored/energy lost per cycle) microwave power, and modulation amplitude were accounted for by the use of chemically stable internal intensity standard.(3) The standard, a ruby crystal (5% Cr^{3+} in Al_2O_3) was mounted permanently in the bottom of the cavity and oriented so as to produce absorption lines at magnetic field intensities both above and below those due to the free radicals of interest.*

A normalized signal amplitude S_n was obtained by dividing the signal amplitude of the residue S_P by the amplitude of the low field ruby line S_R. In the general case where different amplifier gains (G) and modulation amplitudes (M) for the residue and the ruby were used, the normalization expression assumed the

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* The ruby was oriented to yield lines at approximately 1889.0 and 5286.0 gauss with microwave frequency of 9.262 GHz. Free radicals with free spin g values appear at 3304.8 g with the same r-f frequency.

form

$$S_n = \frac{S_P}{S_R} \frac{G_R M_R}{G_P M_P}$$

where the subscripts P and R refer to the primer and ruby, respectively. The signal amplitude of both the residue and the ruby standard was taken as the peak to peak displacement of the first derivative output of the spectrometer.

To avoid problems arising from power saturation of the samples, all measurements were made at 5 mw. This level was established by comparing line shapes in spectra taken over a range of power settings and noting the onset of amplitude distortion. The 5 mw point was below the distortion point in all samples studied.

3. RESULTS

3.1 Introduction

In the sections which follow 3.1-3.5, EPR data are presented for five brands of primer residues. Resonance signals were obtained from the residues of all brands and definite decay patterns could be discerned in three. Sufficiently precise data were obtained for two brands (Peters and Remington) to permit determination of decay constants.

Of the two showing less positive data, one brand (Super Vel) exhibited a usable EPR signal in only one of ten samples studied. All Norma samples, on the other hand, showed very strong EPR signals, but the free radicals associated with them were very stable which (with present techniques) precluded their use in timing studies.

While not of direct interest in the context of establishing time histories of primer residues, it should be noted that the EPR spectra obtained were unique. This finding suggests the applicability of this technique to the identification of residues obtained from such sources as firearms and bombing sites.

3.2 Peters

All primer residues from this source exhibited strong EPR signals. The dominant feature found in the spectra of nine of the ten samples examined was a single broad absorption line at a g value of about 2.0.* This spectral feature (a in Figure 1) proved to be stable at room temperature and was unsuitable for temporal studies. However, a less intense but narrower band also appeared in these samples which did exhibit a measurable decay at room temperature. In six of the nine samples this spectral feature could be resolved sufficiently to permit analysis. This feature is shown at b in Figure 1.

The decay of the total signal amplitude of the b components of samples 15 and 19 are shown in Figures 2 and 3 respectively. In both figures the logarithm of the normalized signal amplitude is plotted against time. As is evident in the figure, the curves can be resolved into two linear components which is consistent with two concurrent first order or psuedo first order processes.**

The half life ($t_{\frac{1}{2}}$) for these processes for the two fully analyzed samples are summarized below.

Sample	$t_{\frac{1}{2}}$ (1)	$t_{\frac{1}{2}}$ (2)
Peters No. 15	1.36 d	276 d
Peters No. 19	1.40 d	183 d

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* The single sample having a markedly different EPR spectrum was obtained from a cup having a 3 prong anvil rather than the usual 2 print anvil. This implies that there is some mixing in the manufacturing process of primers of different compositions intended, perhaps, for different customers (e.g., commercial and military).

** Psuedo first order processes are in fact second order processes in which the concentration of one of the reactants is much larger than the other.(4)

3.3 Remington (Military)

All primer residues studied from this source exhibited very strong EPR absorption. The spectra were all very similar and were characterized by a four component pattern with intensity ratios of about 1:2-4:4. A spectrum typical of this group is shown in Figure 4. While the intensity of all four of these spectral features were found to decay with time, only the third peak (b in Figure 4) was used in the present analysis. This choice was dictated primarily by the more favorable signal to noise ratio found with this feature.

As in the previous case, a plot of the logarithm of the normalized signal amplitude vs. time from discharge could be resolved into two linear components. This is illustrated in Figures 5-10 where signal decays of the six samples are shown. The $t_{\frac{1}{2}}$ for peak b in the six samples analyzed are summarized in Table 3.

An unusually large spread in the early time signal amplitude of sample No. 35 precluded the extraction of the short term decay component in that sample.

It is to be noted that the short term half life in these (Remington) samples is much the same as in the case of the Peters samples, while the long term component is considerably shorter than that found for Peters.

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TABLE 3

SUMMARY OF REMINGTON (MILITARY) PRIMER RESIDUE DATA

Sample Remington No.	Spectral Component b	
	$t_{\frac{1}{2}}$ (1)	$t_{\frac{1}{2}}$ (2)
22	1.05 d	30 d
33	1.55 d	50 d
34	1.63 d	97 d
35	---	66 d
36	1.55 d	58 d
37	1.62 d	92 d

3.4 Western

Primer residues from this source showed the lowest level EPR absorption of all the primer types studied. A spectrum typical of those obtained in all samples from this source is shown in Figure 11. The most pronounced absorption peak (at a in Figure 11) was, in all samples studied, found to decay. Evidence of this decay is clearly seen in Figures 12-15 where the usual semi-log plots of normalized signal amplitude vs. time are given.

Due to the large errors associated with the measurement of these weak signals, it was not possible, however, to extract quantitative decay data in these cases.

3.5 Norma

All six samples studied from this source exhibited strong EPR absorption signals. The spectra, all remarkably similar, were characterized by a single broad absorption band at about 3300 gauss. A spectrum typical of those recorded is shown in Figure 16. The free radicals associated with this absorption proved to be stable (at room temperature) as no diminution in signal amplitude was observed after times up to 20 days after firing.

3.6 Super Vel

Of a total of ten samples examined from this source, one exhibited a strong EPR absorption signal. The absorption in the remaining nine was judged to be too weak to be analyzed under the existing experimental conditions.

The EPR spectrum of the sole strongly absorbing sample is shown in Figure 17. A strong double line is noted at approximately g = 2. The decay of this sample, shown in Figure 18, was unlike that of any of the others investigated in this program.* As can be seen in the future, the signal increased in amplitude for the first three days after which a typical decay pattern developed.

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* Similar behavior was noted in a CCI powder residue.(5)

4. DISCUSSION AND INTERPRETATION

The results of these investigations strongly suggest that zero times can be extracted from the free radical decay curves of primer residues. In certain instances zero times can be extracted through a direct application of results of these investigations although, in general, additional characterization is required. The remainder of this section is devoted to illustrating how decay data from Peters and Remington Military residues can be utilized to obtain zero times. This same basic approach should be applicable to all residues having similar decay kinetics.

Because of the two-component nature of the decays in the Peters and Remington Military residues, it is convenient to divide the post firing period into prompt ($t_o \leq 5$ day) and delayed ($t > 5$ day) time segments. The fact that the decay is two component immediately suggests that bounds can be placed on the zero time from the gross shape of a decay curve; a single slope decay indicating $t_o > 6$ days, a two slope decay indicating $0 \leq t_o \leq 6$.

More quantitative zero time data can also be obtained in both time regimes. In the prompt time region, where the signal decay curve is resolvable into two linear segments, t_o can be obtained from the short and long half life amplitudes $S_1(t)$ and $S_2(t)$, respectively (see Figure 3). This is illustrated in Figure 19 where the logarithm of the ratios $S_1(t)/S_2(t)$ for Peters samples 15 and 19 are plotted as a function of post firing time. Using these curves as a standard, the t_o of a test sample is determined directly from its $S_1(t)/S_2(t)$ value by finding the time coordinate of its intercept with the standard curves. For example, a Peters sample with an S_1/S_2 of 0.2 is found to have a Δt value of 1.7 ± .15 days. Figure 20 suggests that a similar analysis may be applied to prompt Remington Military residues, although in this case evidence of different patterns within the sample residue type are present.

In the case of delayed samples, it will be necessary to extrapolate the long half-life component back to a predetermined level of the initial value of $S_2(t)^*$ to effect a zero time determination. Assuming the zero time value of S_2 to be known, the semi-log plot of normalized signal amplitude vs. time could be extrapolated to the value of S_2 at t_o, $S_2(t_o)$. As may be apparent, this method of determining zero times is applicable to both prompt and delayed samples. In the prompt case, the extrapolation method could provide data to supplement that from the approach previously outlined. At this stage of the investigation reliable zero time amplitudes $S_2(t_o)$ are not yet available. Study and the verification of this technique must await further data.

The data from the remaining residue types were not amenable to analysis either because of instrument insensitivity (Western)

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* More precisely, the appropriate S_2 value would necessarily be normalized to a unit mass.

and Super Vel), or free radical stability (Norma). It is believed that with modest improvements in instrumentation, particularly in regard to sensitivity, that Western samples could be analyzed in the manner outlined for Remington Military and Peters.

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APPENDIX

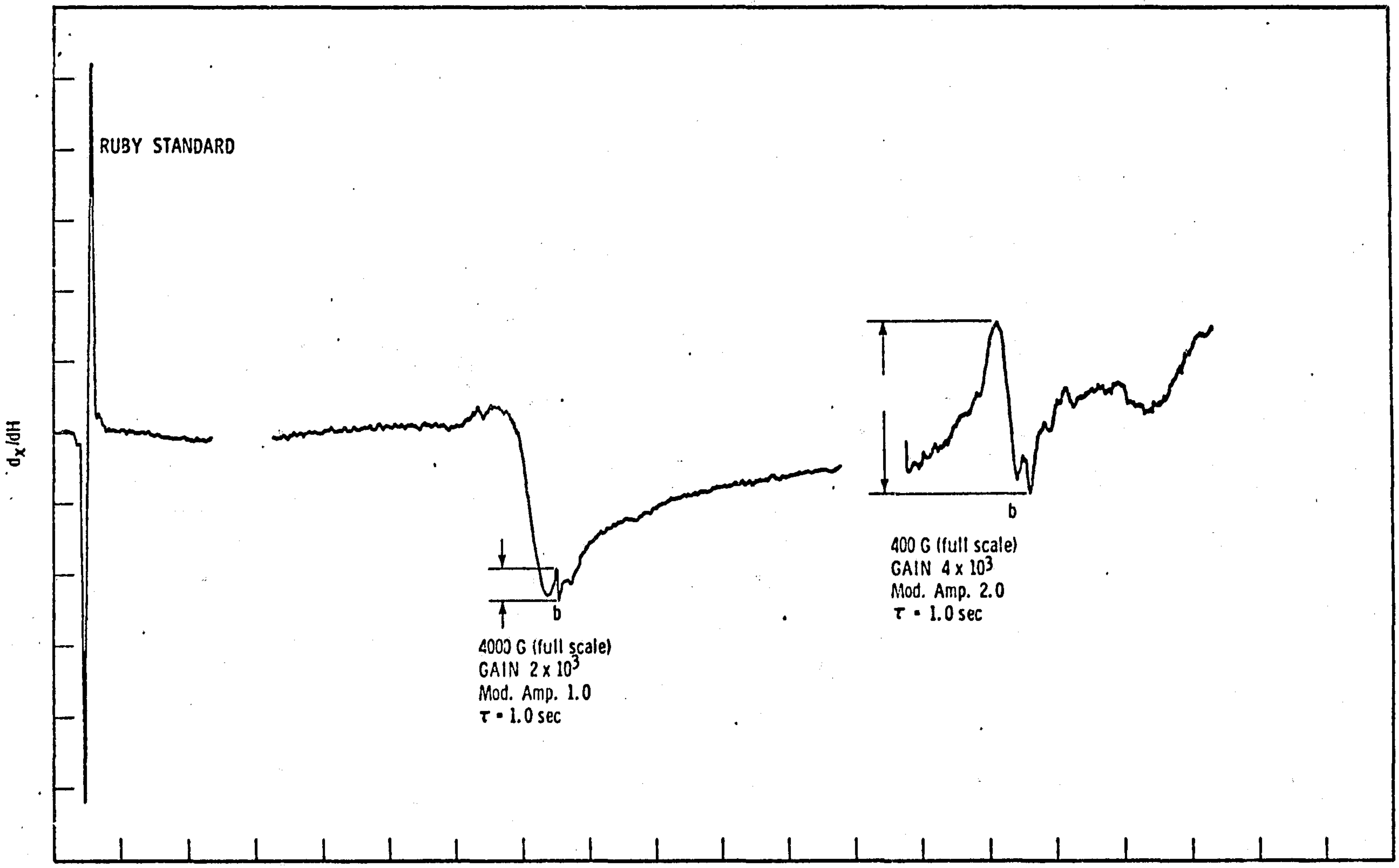

Fig. 1. Typical EPR spectrum of Peters primer residue.

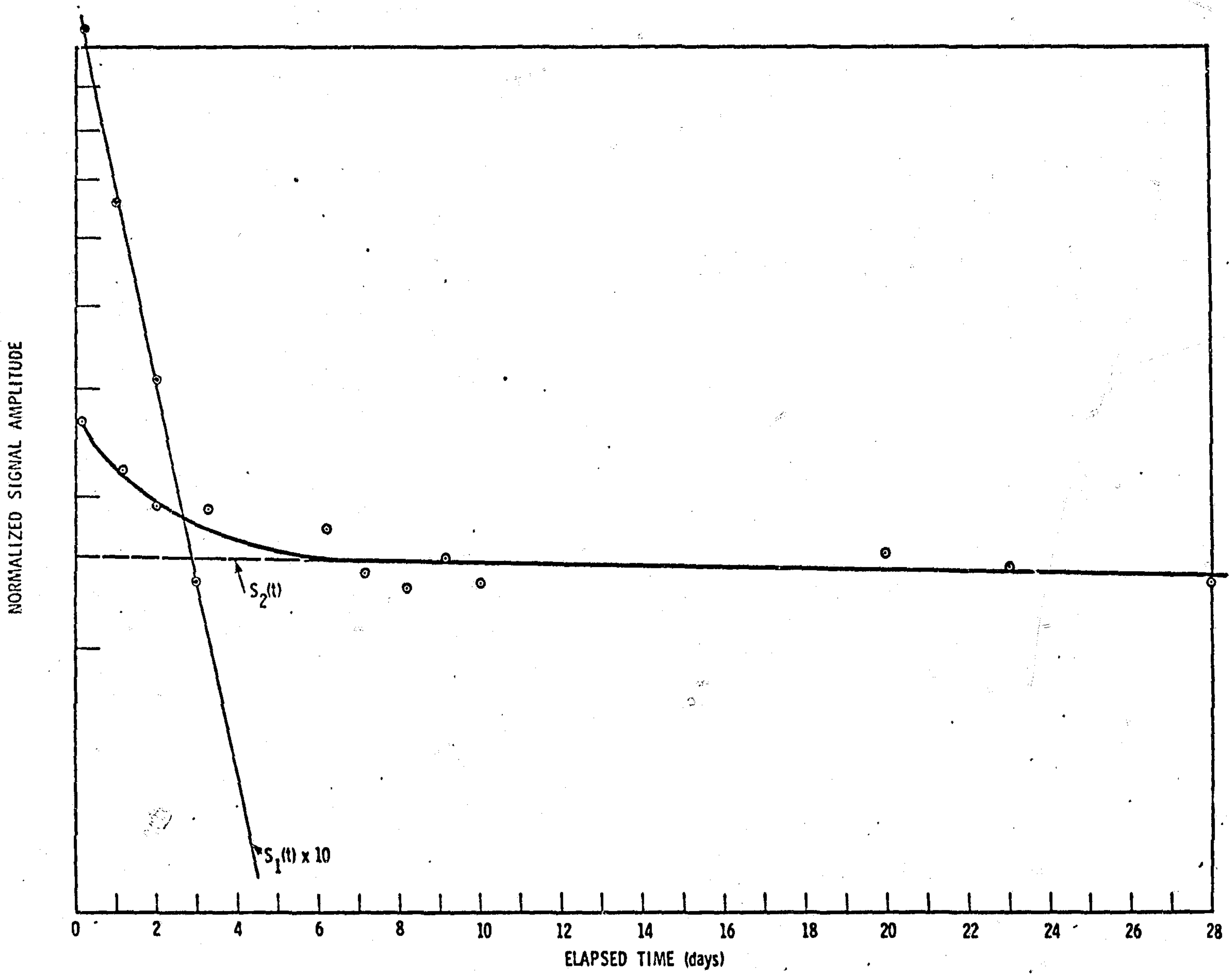

Fig. 2. EPR signal amplitude of Peters sample 15 as a function of time after firing.

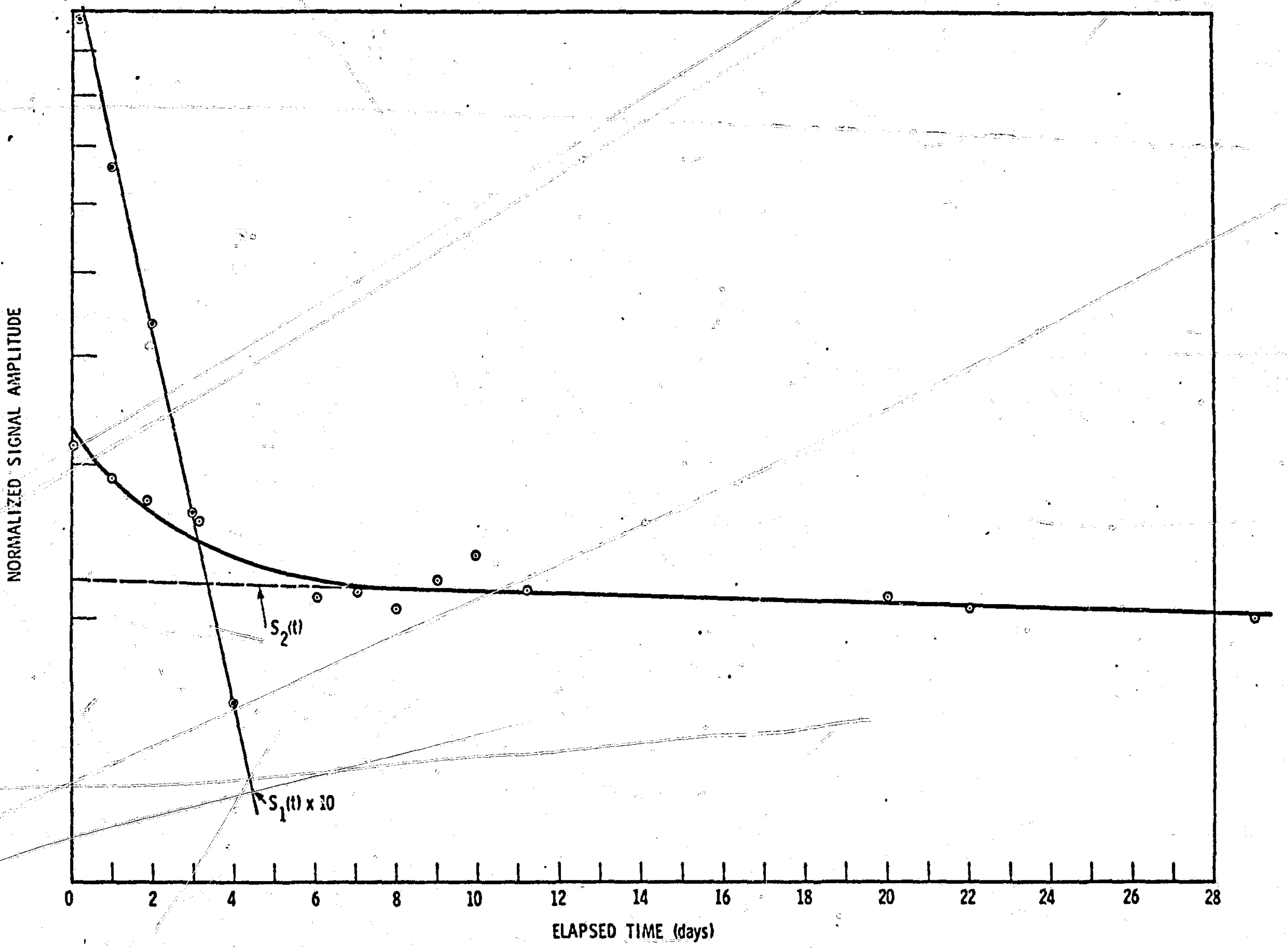

Fig. 3. EPR signal amplitude of Peters sample 19 as a function of time after firing.

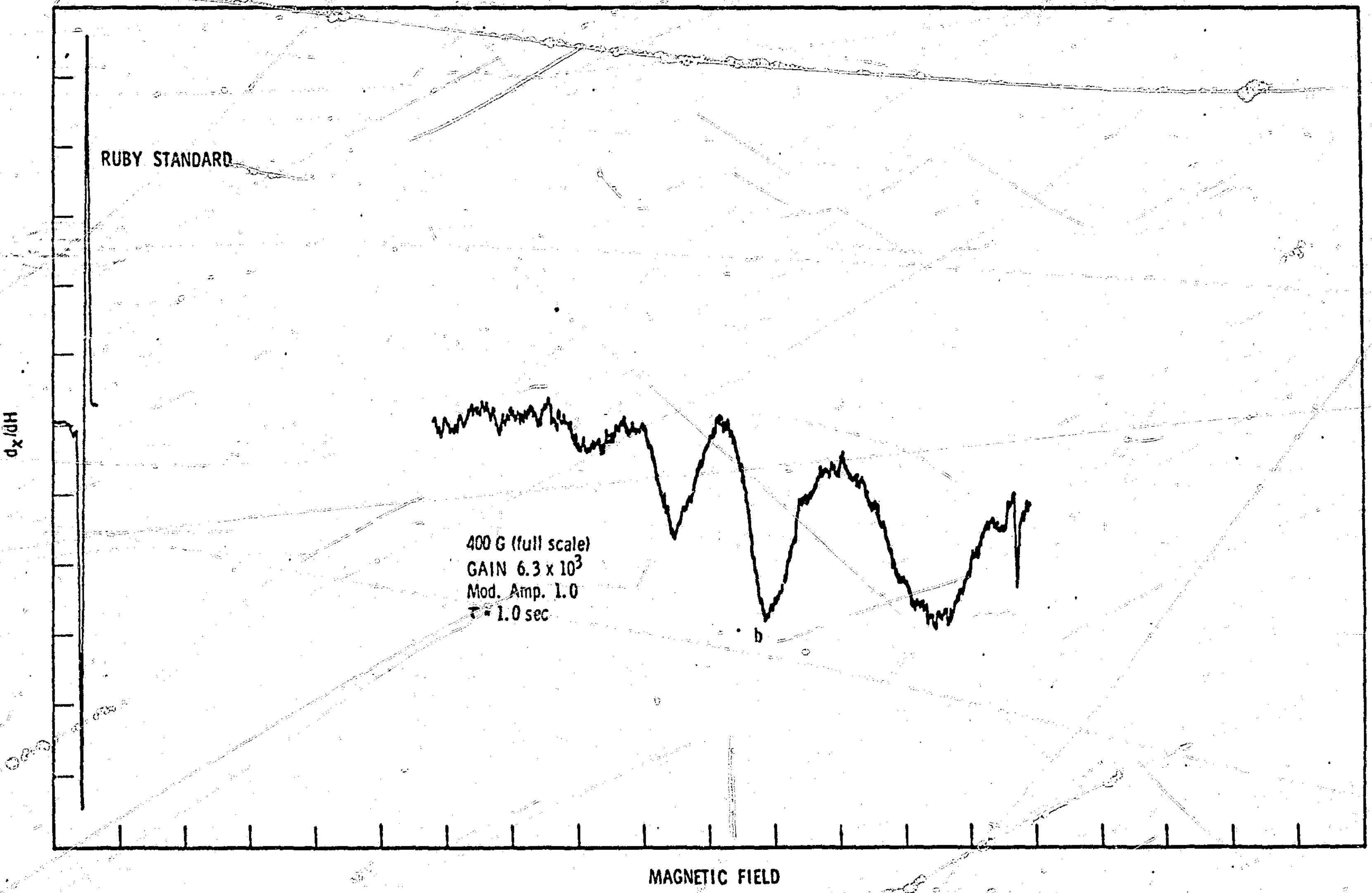

Fig. 4. Typical EPR spectrum of Remington (military) primer residue.

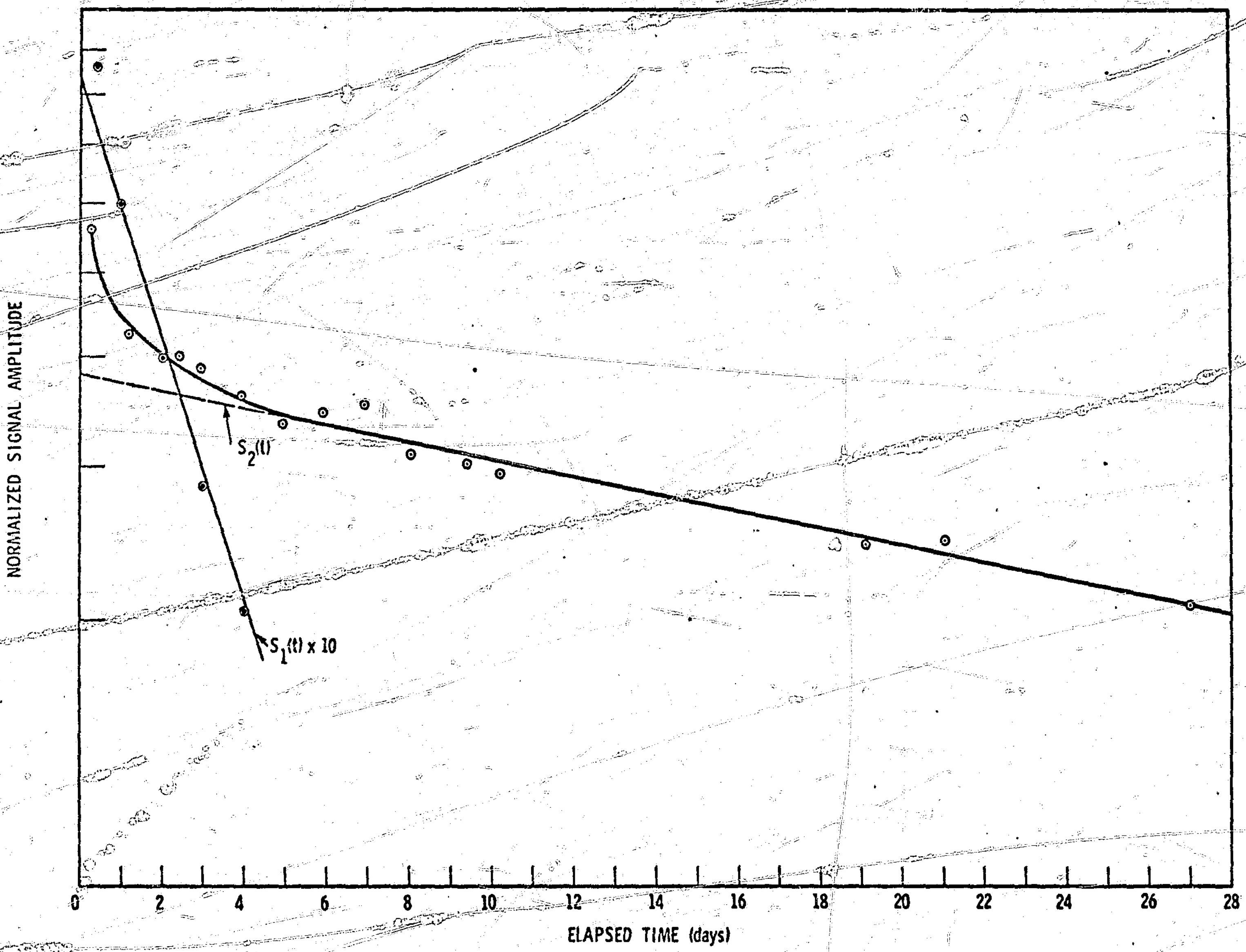

Fig. 5. EPR signal amplitude of Remington sample 22 as a function of time after firing.

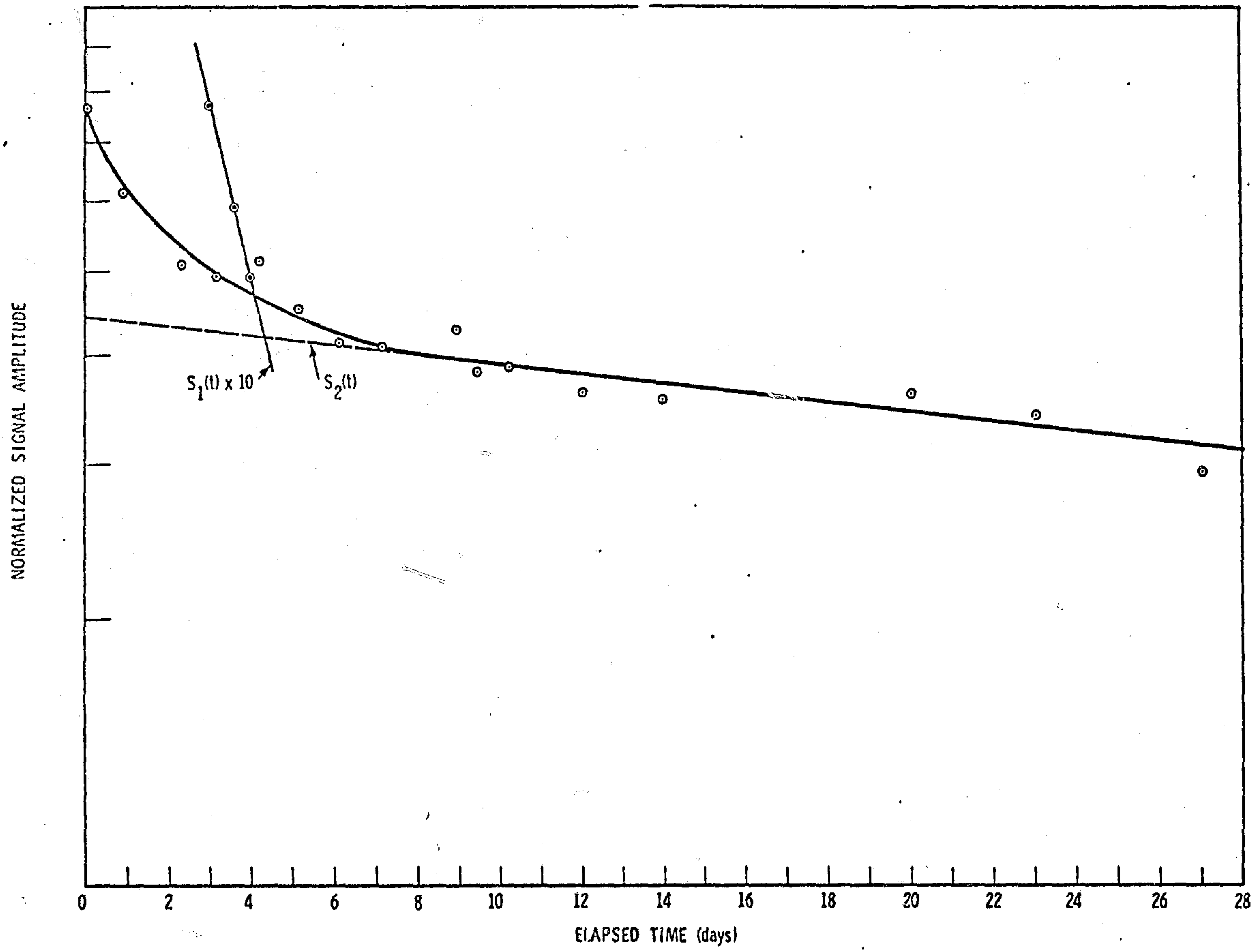

Fig. 6. EPR signal amplitude of Remington sample 33 as a function of time after firing.

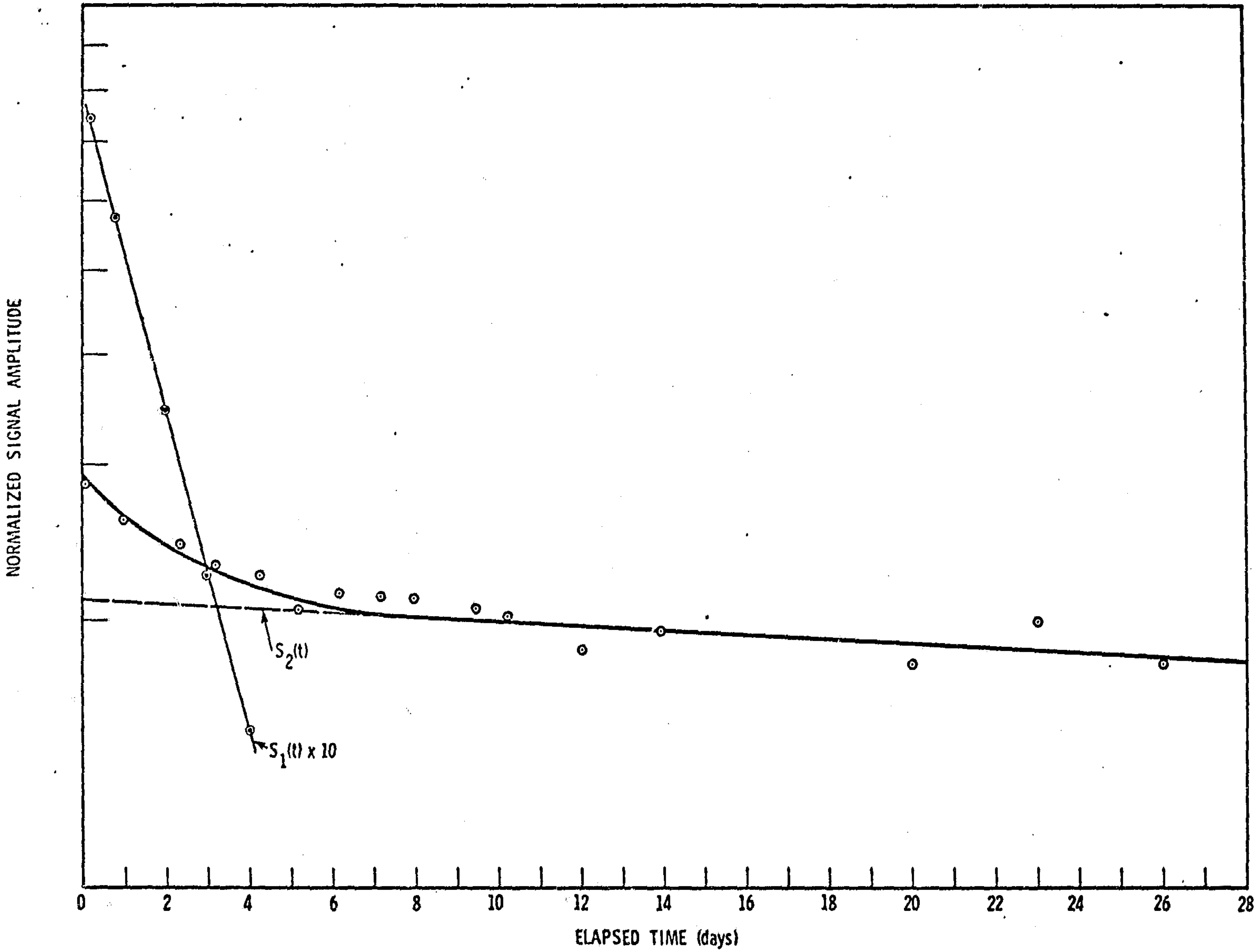

Fig. 7. EPR signal amplitude of Remington sample 34 as a function of time after firing.

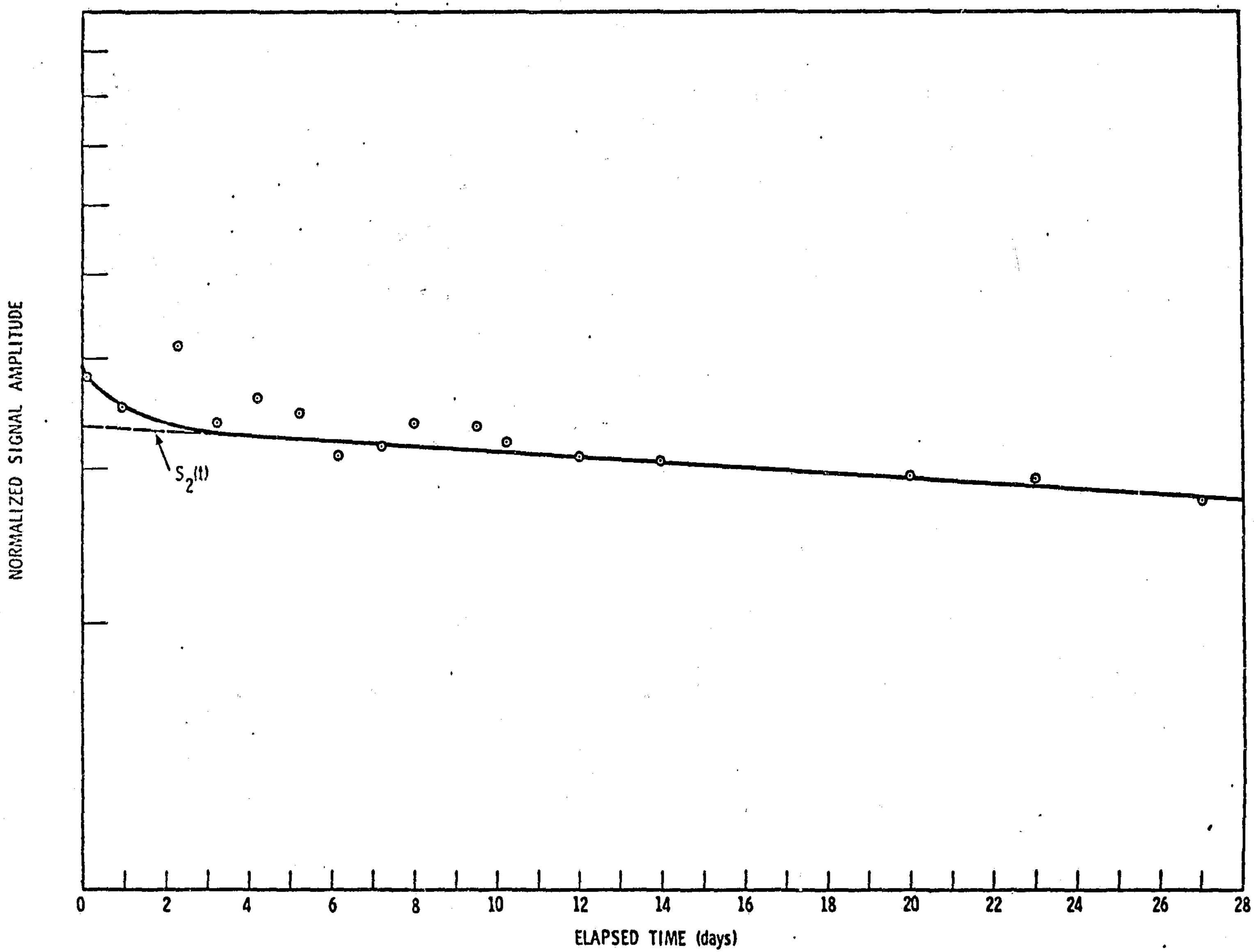

Fig. 8. EPR signal amplitude of Remington sample 35 as a function of time after firing.

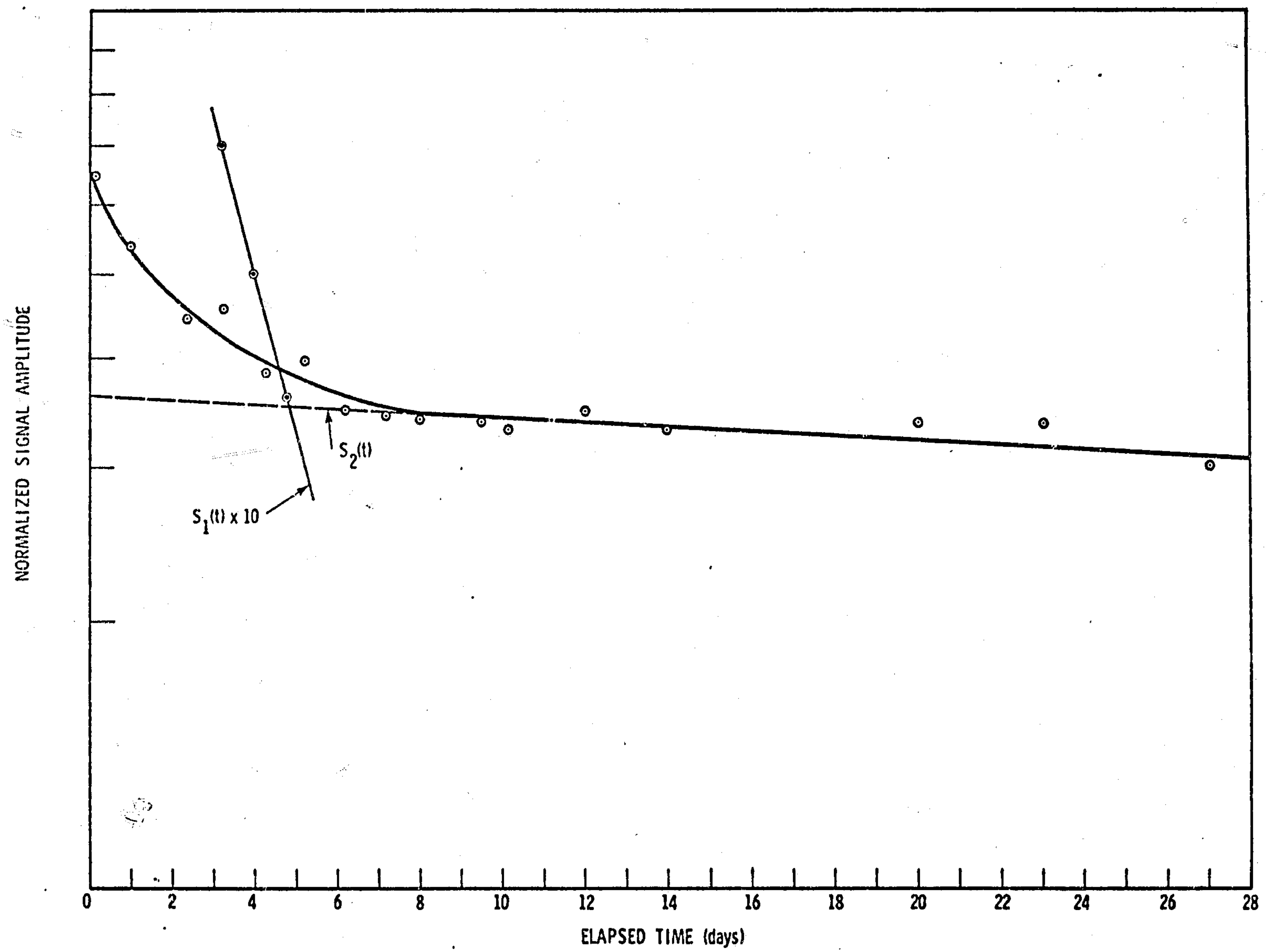

Fig. 9. EPR signal amplitude of Remington sample 36 as a function of time after firing.

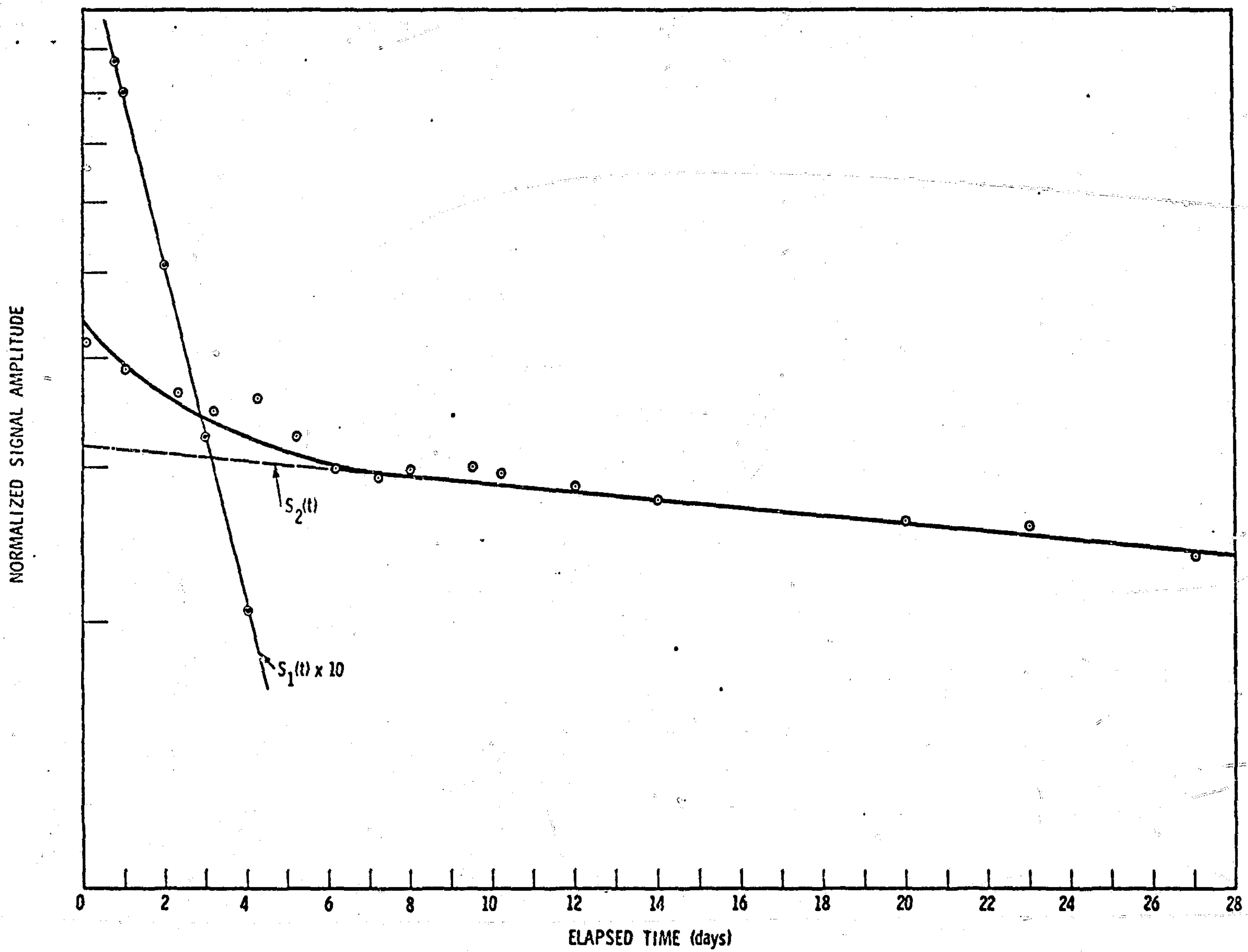

Fig. 10. EPR signal amplitude of Remington sample 37 as a function of time after firing.

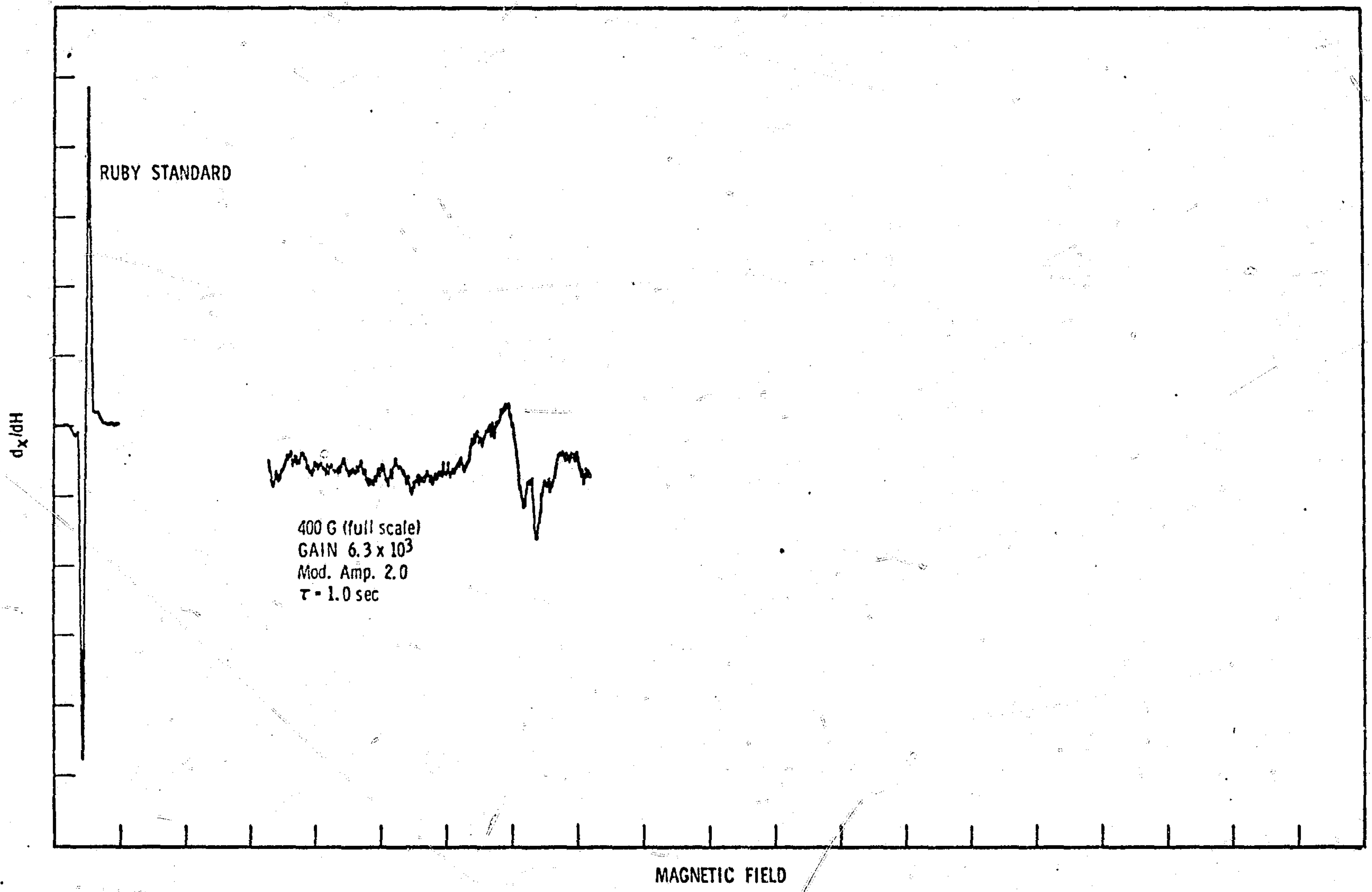

Fig. 11. Typical EPR spectrum of Western primer residue.

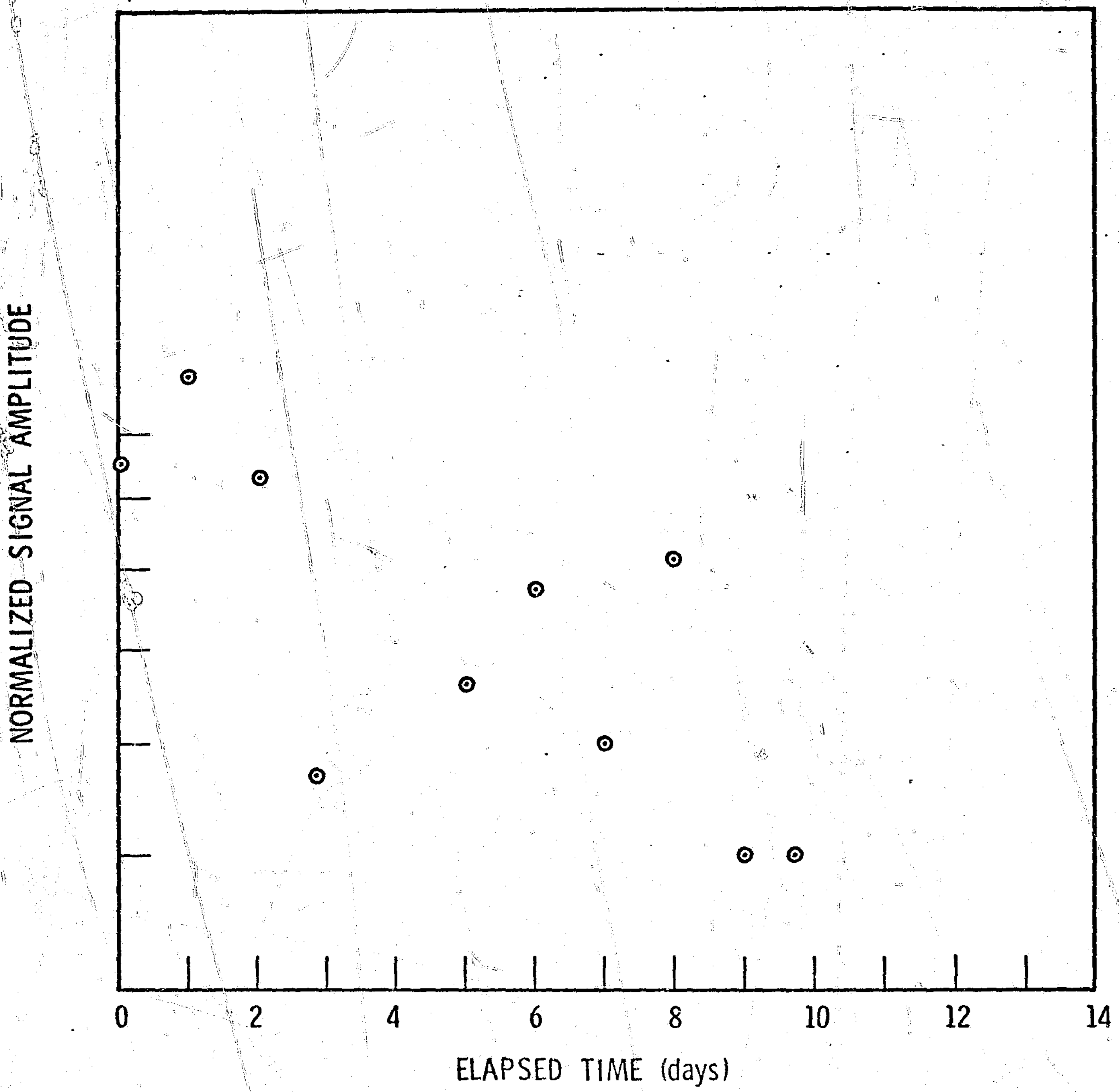

Fig. 12. EPR signal amplitude of Western sample 29 as a function of time after firing.

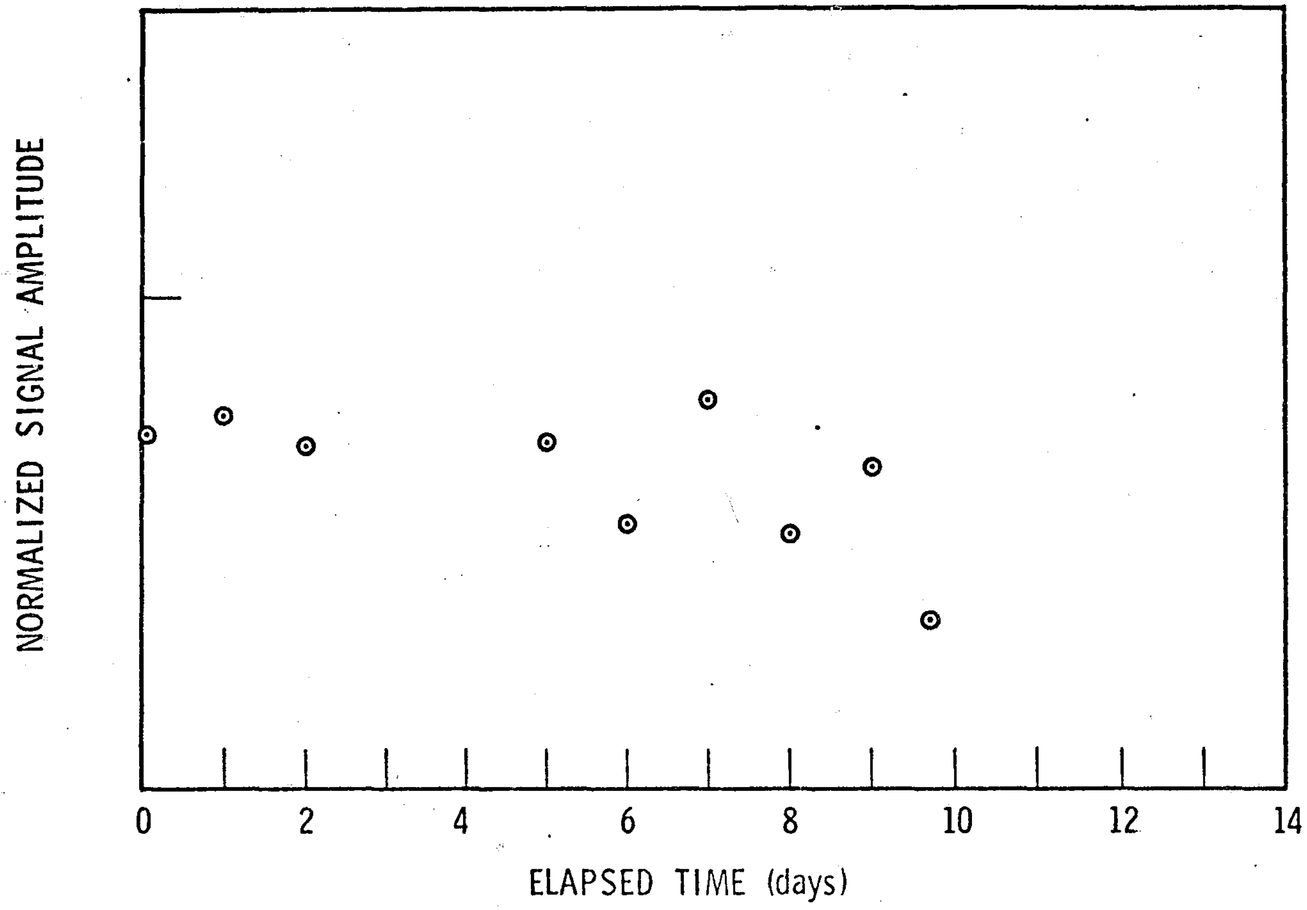

Fig. 13. EPR signal amplitude of Western sample 30 as a function of time after firing.

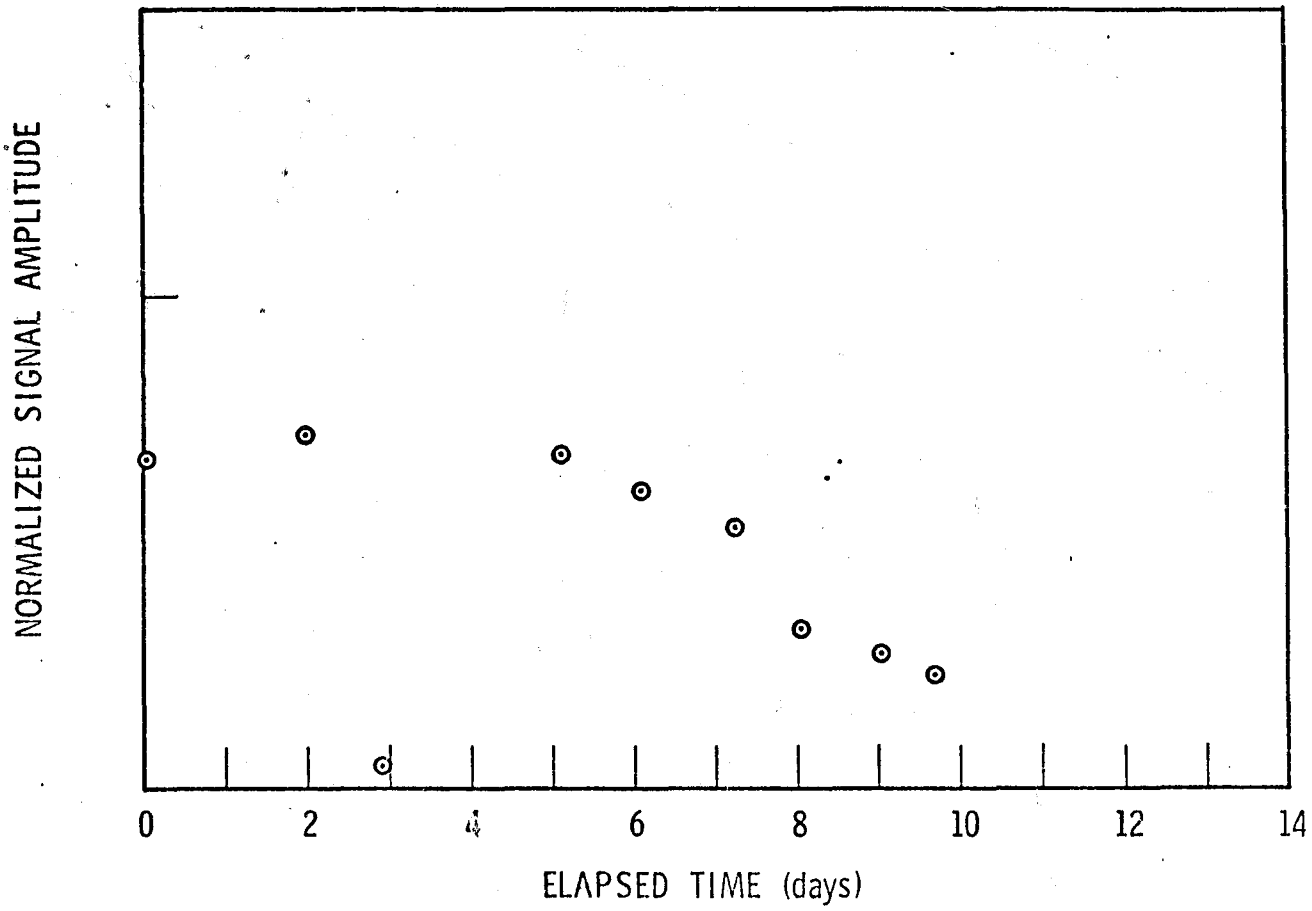

Fig. 14. EPR signal amplitude of Western sample 31 as a function of time after firing.

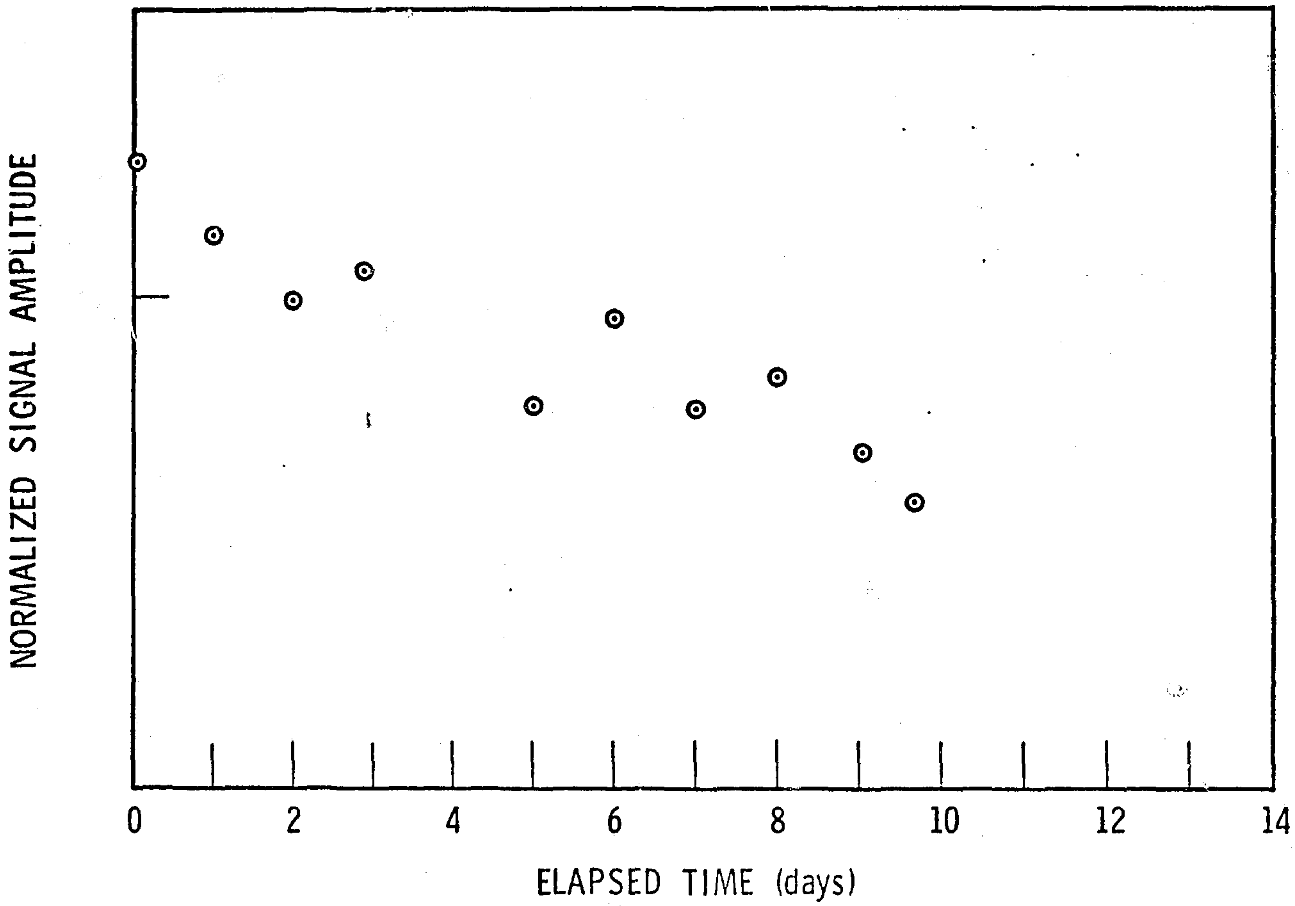

Fig. 15. EPR signal amplitude of Western sample 32 as a function of time after firing.

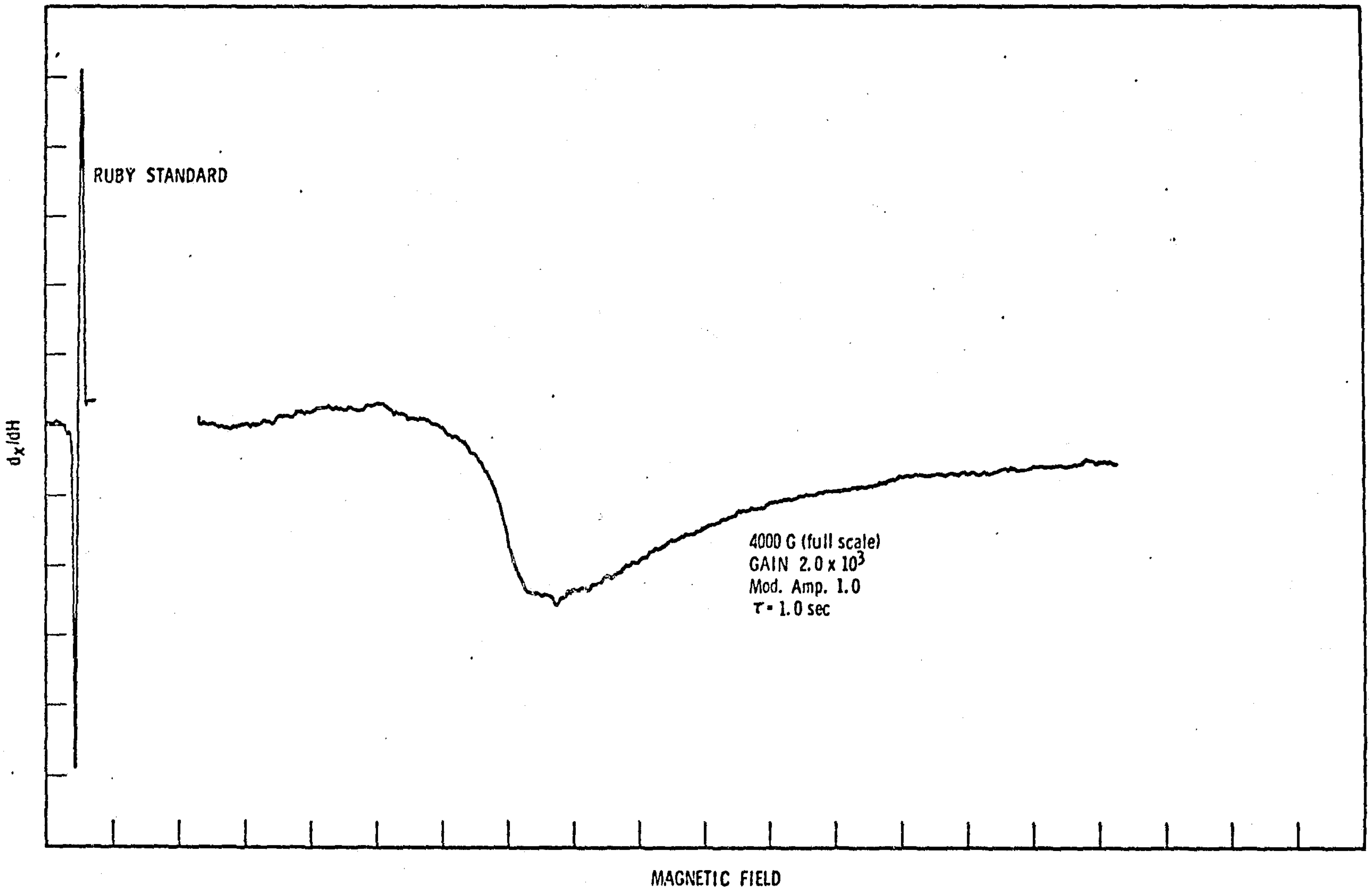

Fig. 16. Typical EPR spectrum of Norma primer residue.

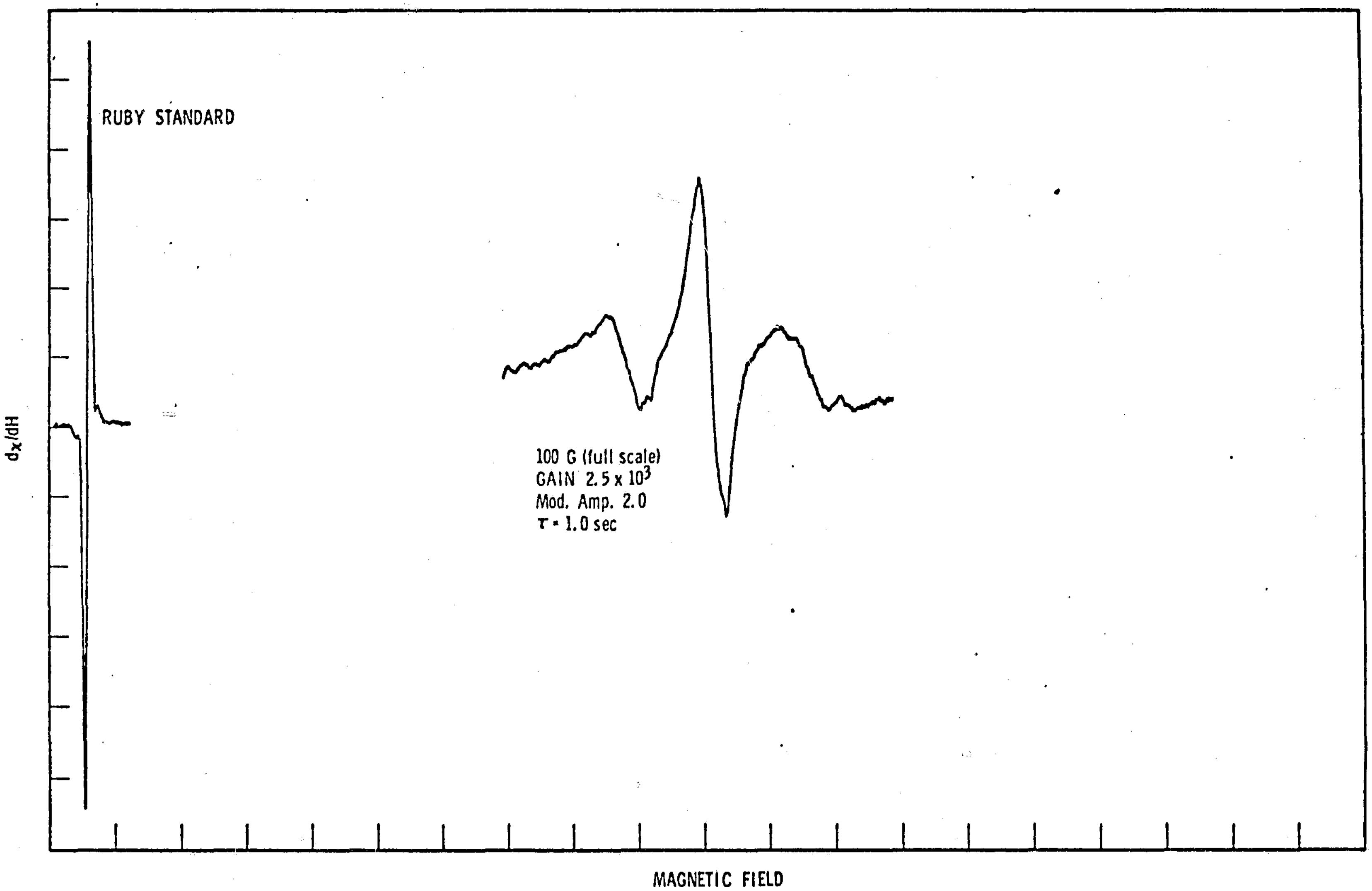

Fig. 17. EPR spectrum of Super Vel primer residue (sample 38)

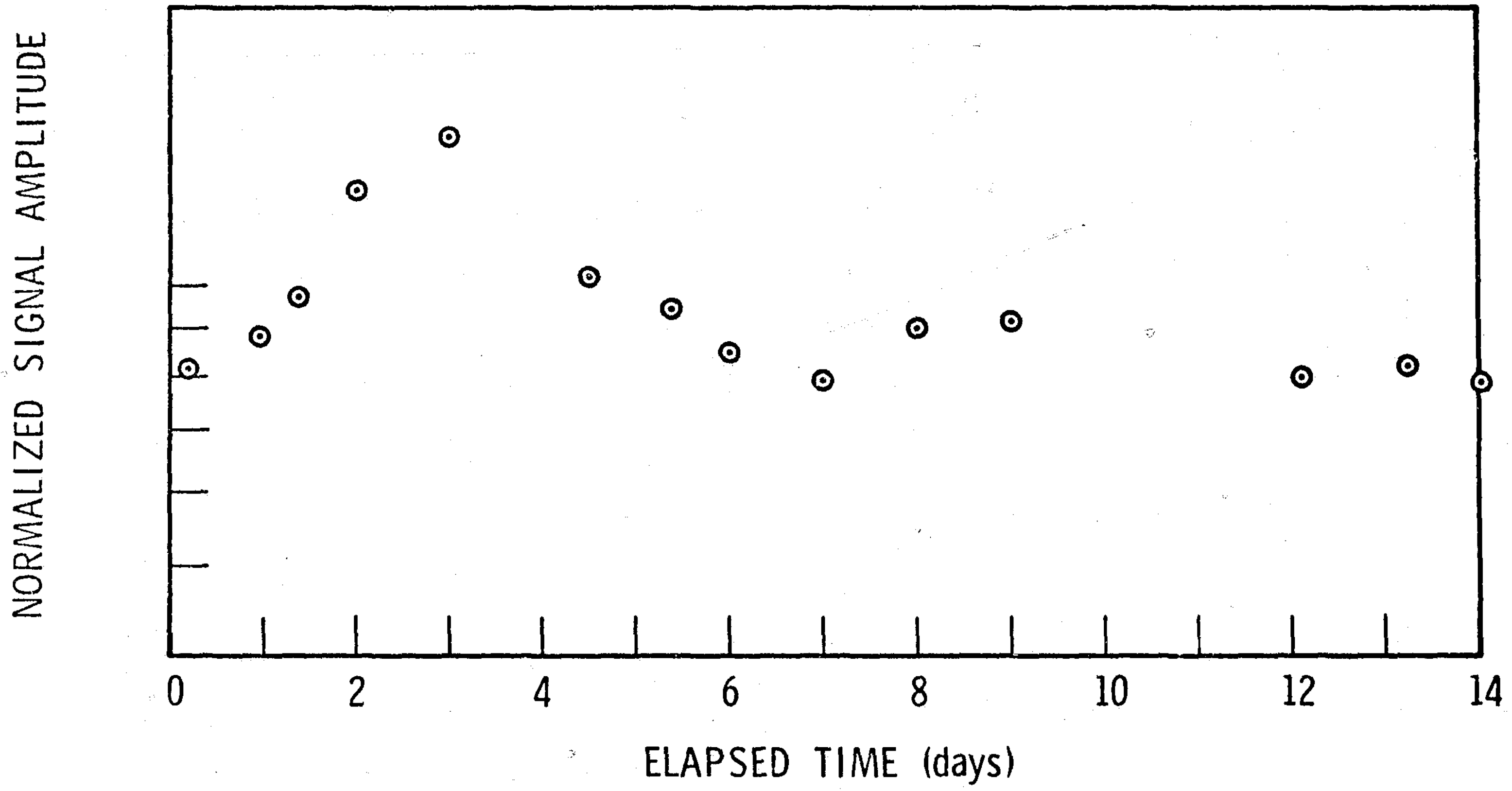

Fig. 18. EPR signal amplitude of Super Vel sample 38 as a function of time after firing.

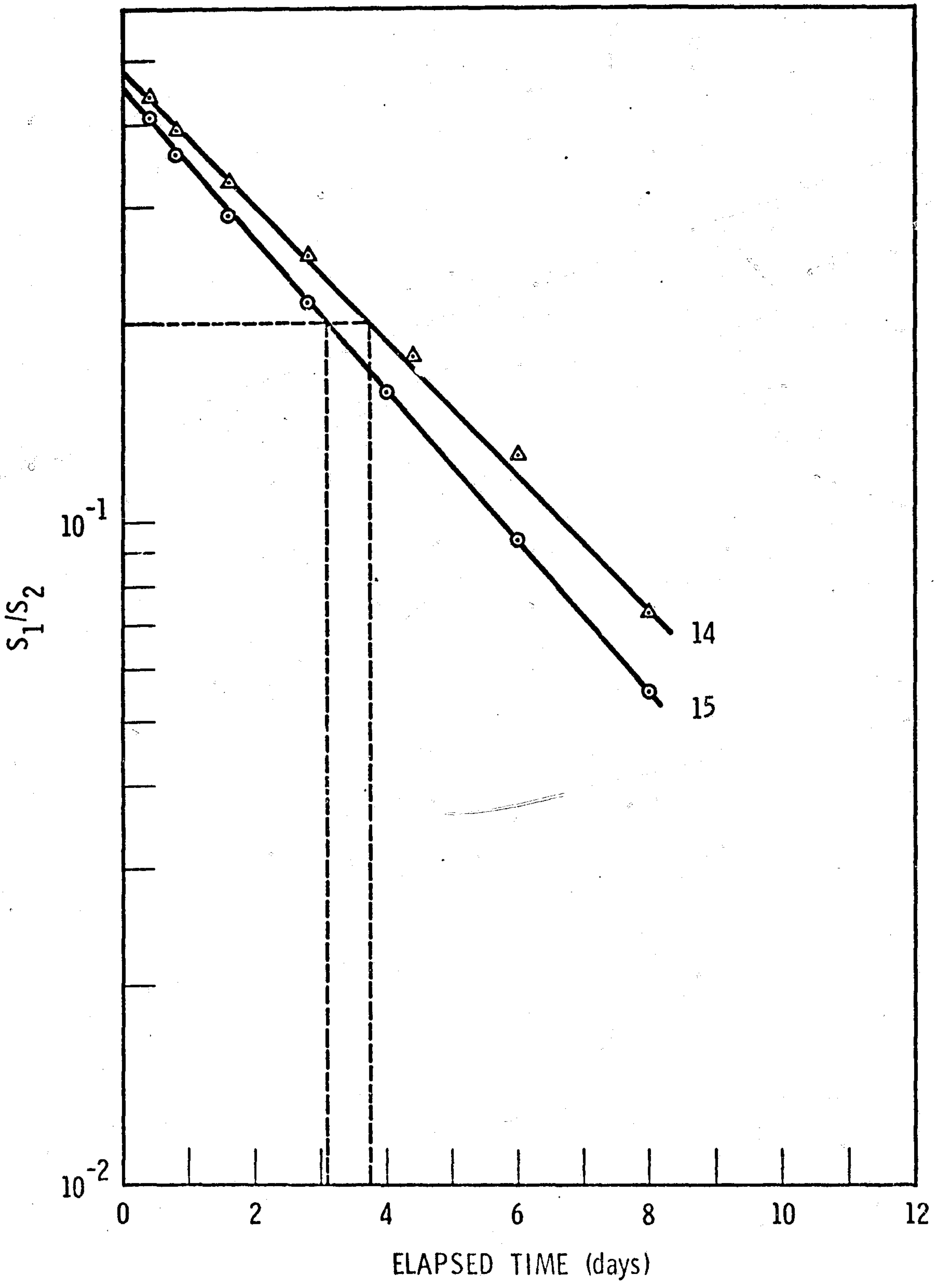

Fig. 19. Ratios of signal amplitudes S_1 and S_2 for Peters samples 15 and 19.

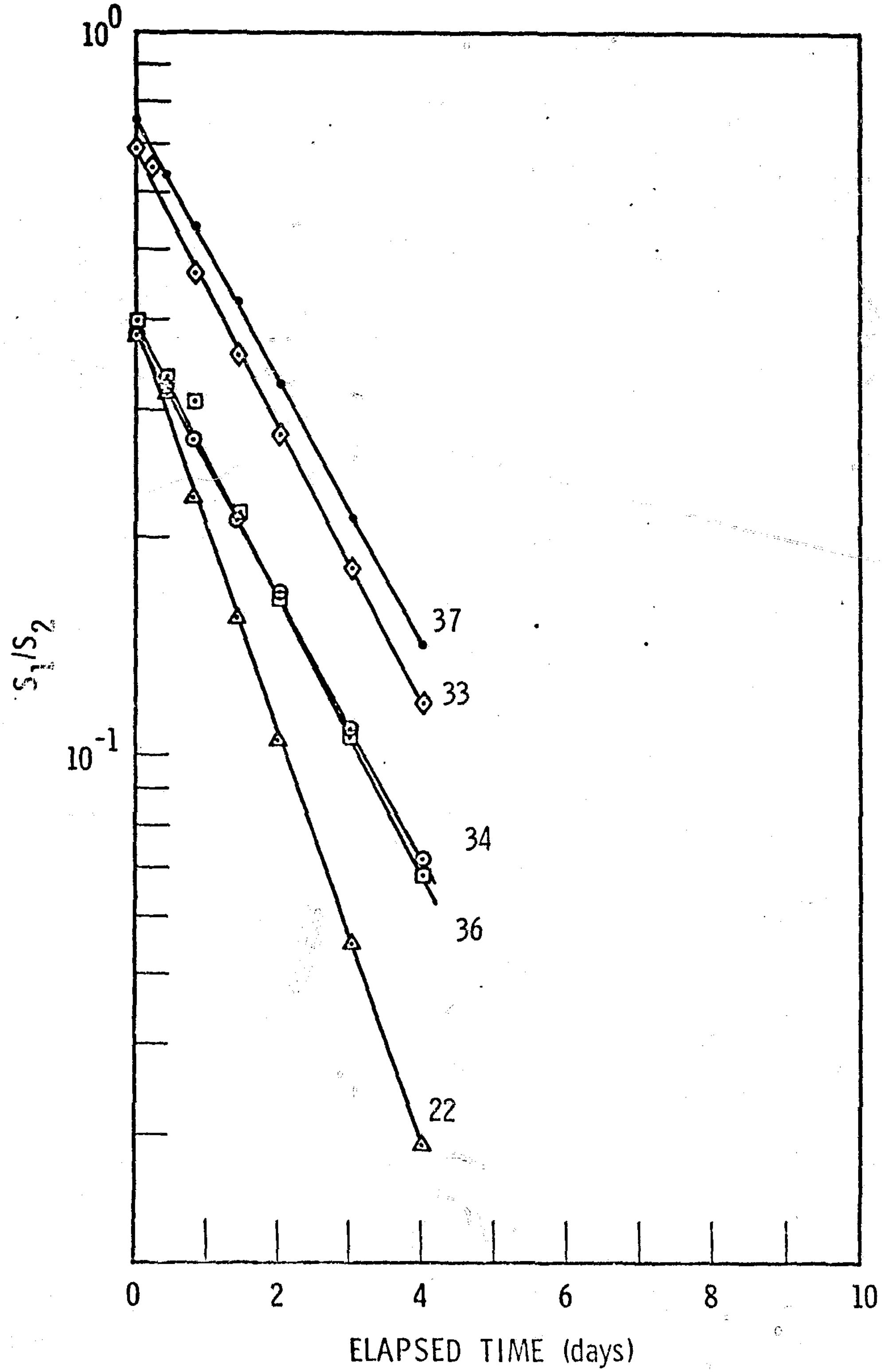

Fig. 20. Ratios of signal amplitudes S_1 and S_2 for Remington samples 22, 33, 34, 35, 36, and 37.