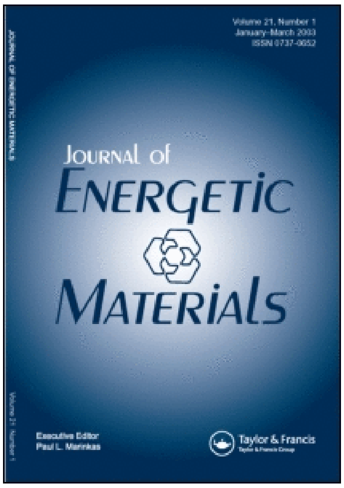

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II. Sensitivity and reliability of the discontinuous vacuum stability test

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GAS EVOLUTION ANLYSIS

II. SENSITIVITY AND RELIABILITY OF THE DISCONTINUOUS VACUUM STABILITY TEST

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ABSTRACT

Gas evolution, due to phase expansion, remains an attractive and sensitive method for stability evaluation. Unfortunately, this technique is also sensitive to errors. Numerous factors such as pressure, volume, temperature, volatiles, and solubility, may significantly affect the results. The effect of such factors is evaluated. A better control of the test conditions prevents errors and makes the discontinuous VST a fast and accurate technique for stability/compatibility evaluation.

INTRODUCTION

Accelerated aging is an attractive method since the time of such a test is reduced to the order of a few days. Unfortunately there is a price to pay: a loss in accuracy of the results. The accuracy relies on both the process of aging and the method used to measure the result of this aging. Modern analytical methods tend to reduce instrumental errors. However they may not be sensitive enough to detect the small chemical change associated with chemical degradation. A degradation of less than 1% in propellant ingredients may be critical for the stability of the composition.

Gas evolution, on the other hand, is extremely sensitive in that it takes advantage of the volume expansion associated with the phase change from condensed to vapour state. Unfortunately, gas evolution methods are extremely sensitive to errors.

Numerous factors such as sampling, degassing, volatiles, temperature, pressure, headspace volume, solubility of gases(1), airtightness, and condensation, were found to be potential sources of errors. Test methods in which these problems cannot be mastered will produce inaccurate results.

The objective of this study was to identify most of the sources of errors in order to eliminate or reduce them and take advantage of the sensitivity of the gas evolution method.

The chemical stability test consists in accelerating the decomposition reaction by heating a representative sample and measuring the amount of gas evolved ($V_{measured}$). The volume of gas representative of the degradation reaction ($V_{degrad.}$) is given by the relation:

$$V_{degrad.} = V_{measured} - \Sigma dV_i \qquad (1)$$

where ΣdV_i is the sum of all the errors associated with: 1) the method of aging (representativity of the accelerated aging), 2) the stability test method, and 3) the experimental method (instrument).

1. METHOD OF AGING

Aging temperature effect

According to the Arrhenius law, a chemical reaction rate increases with temperature (figure 1). Thus, a chemical degradation reaction which may take years at room temperature, is reduced to the order of a few days at high temperature. However one may question how representative is this accelerated aging as different decomposition mechanisms may take place at high temperature(2). Therefore, it would appear that the lower the temperature, the more realistic is the stability test. The problem with using low test temperatures is that the test duration must be increased to compensate for lower gas evolution.

Autocatalytic effect

The VST applies to any materials whose chemical degradation produces gaseous products such as H_2, O_2, N_2, CO_2, and NO_x. Vacuum allows these gases to be removed from the sample and to be collected in the tube. Under normal storage conditions, chemical degradation of nitrate esters is accelerated by the formation of free radicals(3). How effective is this autocatalysis in a vacuum tube, where gaseous species are partially removed from the material, especially when the sample is small? Figure 2 shows that the autocatalytic effect for AN-TMETN mixture is still important. However, this effect is less pronounced in the case of TMETN alone, as illustrated in figure 3. The larger the sample, the more realistic is the vacuum stability test.

Linear process versus non linear process

According to equation 1, the stability test result is valid only if we have an accurate control not only on the stress applied but also on all of the parameters involved such as the pressure (P), the temperature (T), the free volume (V_f), and the solubility of gases in the sample (S).

<u>Initial conditions</u>　　　　　　<u>Final conditions</u>

(P, T, V_f, S,...)　　　　　　(P, T, V_f, S,...)

Sample $\xrightarrow[\text{heat}]{}$ Aged sample + evolved gas

The question is : what should be the accuracy with which we must control these parameters in order to obtain an accurate and reproducible result? Generally, when a process is simple and linear, slight inaccuracies of the initial conditions will not affect the final result. The process of pouring a liquid through a funnel is a typical example of such a linear and simple process.

In contrast, when the process is complex and non-linear, the result depends strictly on the process conditions. Any uncertainty of the initial parameters could be amplified and may result in an erroneous result. A VST experiment, where the volume of evolved gas varies exponentially with temperature (figure 1) and depends on numerous parameters, is a typical example of a complex and non-linear process. In this case, tests results are reproducible only if the parameters are controlled with accuracy.

2. ERRORS ASSOCIATED WITH THE STABILITY TEST METHOD

Weight effect

To assess the influence of sample weight on the results, stability tests on different weights of AN/BDNPAF mixture were performed. We found that the volume of evolved gas increases when the weight decreases, as indicated in table 1.

TABLE 1 . Effect of tube volume and sample weight on gas evolution for AN/BDNPAF mixture at 100°C for 48 hours. (AN is stabilised by 3% ZnO)

Weight (g)	Tube volume (ml)	Volume of gas (ml/g)
Effect of volume (same weight)		
2.024	52.23	2.15
2.032	50.74	2.14
2.028	50.21	2.13
2.009	28.97	1.88
2.027	26.93	1.83
2.011	29.70	1.81
Effect of weight (approximately the same volume)		
1.535	50.74	2.29
2.996	54.03	1.96
4.404	53.13	1.74
9.953	50.20	1.23

Free volume effect

Unavoidable deviations in the volume of the tubes had a significant influence on the results. Experiments performed on the same sample but in different free volumes provided different results, although the reproducibility for each volume is excellent, as illustrated in table 1.

Solubility effect

Both the volume and weight effects could be explained by solubility of gases in the sample (the gas remaining in the sample does not contribute to the pressure in the gas phase). As solubility depends on both the free volume and the sample weight, this dependence is better expressed by the combined factor of dilution V/w. The solubility effect is confirmed by the results shown in figure 4, where the volume measured is plotted versus the factor of dilution V/w. The VST results were significantly underestimated since the actual volume is equal to the sum of the volume measured and the volume due to solubility. The curve shows, however, that for dilution factors higher than 50, the solubility effect is negligible.

Adsorbed gas and volatiles

These may significantly increase the volume of gas evolved. Figure 5 shows the presence of traces of acetone in BTTN which was not thoroughly degassed. In order to eliminate the volatiles, the material and the glass tube must be degassed thoroughly by repeated pumping and desorbing at high temperature.

Homogeneity

This is also a requirement when we deal with composite material. Inhomogeneity may be caused by solid sedimentation during the curing of the cast material. It may be prevented by sampling vertically.

3. ERRORS ASSOCIATED WITH THE INSTRUMENT

Air-tightness

Any leak would ruin the test. The ground glass joint, the valve and the septum, which are the only possible sources of leaks, proved to be air-tight since a variation of less than 2 torr is observed when a test control is run at 100°C for 48 hours.

Gas condensation

With the mercury method, the top of the tube and the capillary tube are not heated, resulting in gas condensation and erroneous results. With the discontinuous method, condensation is prevented since the entire tube is at the test temperature.

Pressure and temperature corrections

Since the tube and the PT are at the same temperature (ambient) when the pressure is measured, there is no need for temperature correction. The PT provides absolute pressure and pressure correction is not required.

Temperature effect

The higher the temperature, the less linear is the degradation process as shown in figure 1, where the volume of gas evolved is plotted versus temperature. At 100°C the Arrhenius law has a magnifying effect and the final results depend on the experimental parameters. Temperature is certainly the most critical parameter and must be controlled within 0.01°C. Temperature gradients must be avoided for the same reasons.

Other parameters such as diffusion of gases and vapour pressure, not considered in this study, may also affect the results.

CONCLUSIONS AND RECOMMENDATIONS

Gas evolution analysis depends on numerous parameters such as temperature, pressure, headspace volume, solubility of the gaseous products in the sample, and volatiles. Understanding and controlling each parameter are major requirements for reliable and accurate results. Temperature is the most critical parameter for the aging and test methods. It is advantageous to lower the aging temperature. This will, unfortunately, decrease the gas evolution (figure 6). This inconvenience is overcome by running a larger sample and increasing the test duration (long term stability test).

The discontinuous VST described in part I, meets the requirements for reliability and accuracy.

ACKNOWLEDGEMENTS

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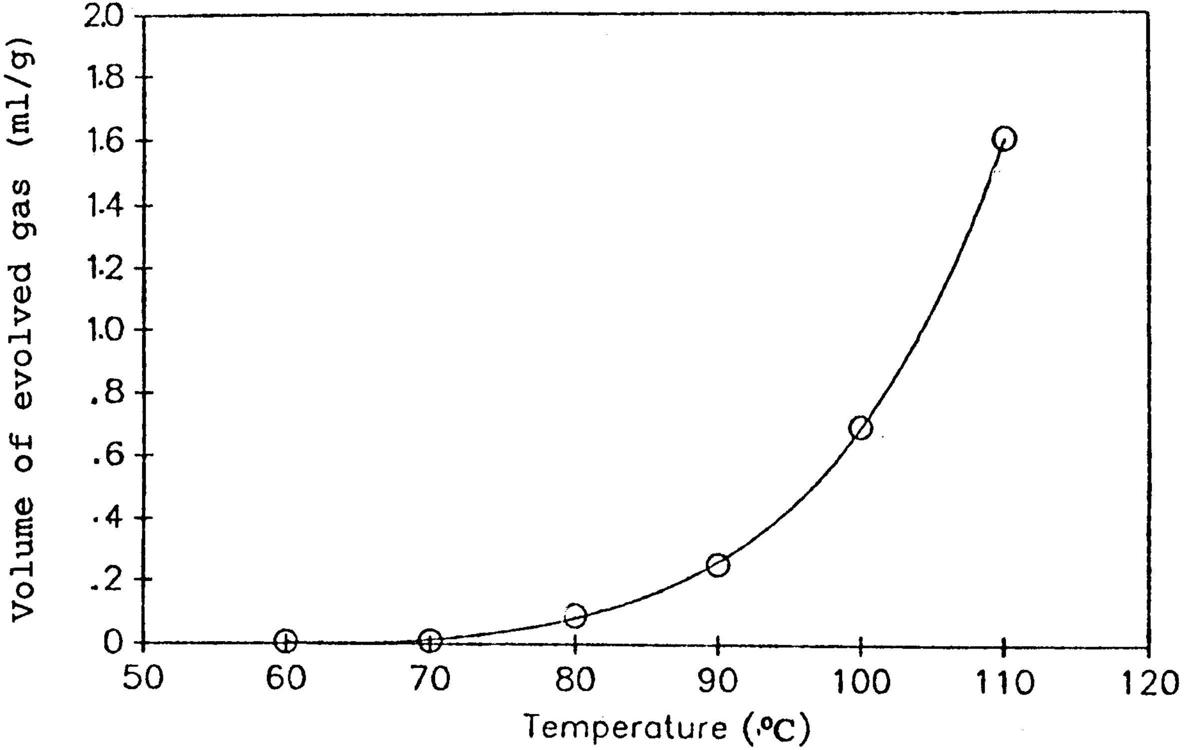

FIGURE 1
Gas evolution as a function of temperature for TMETN over two days.

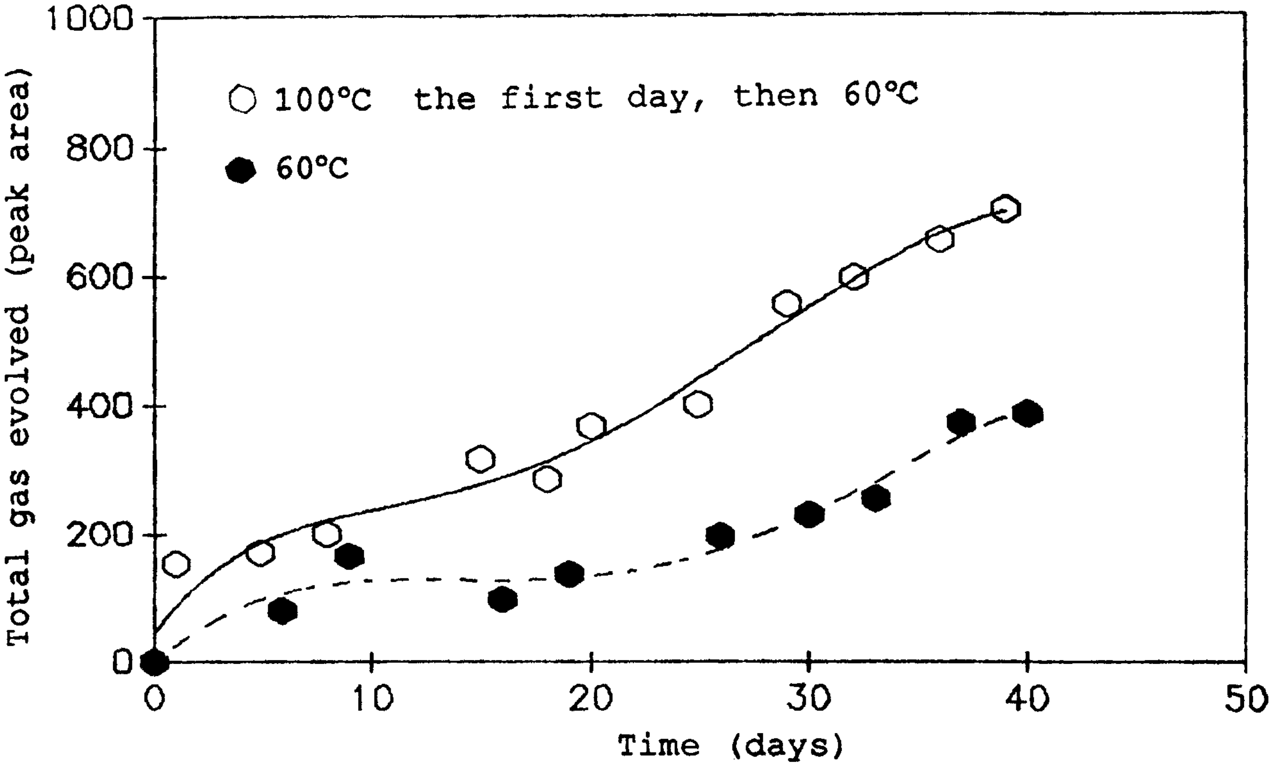

FIGURE 2
Autocatalytic effect of NO_2 on the decomposition of AN/TMETN mixture.

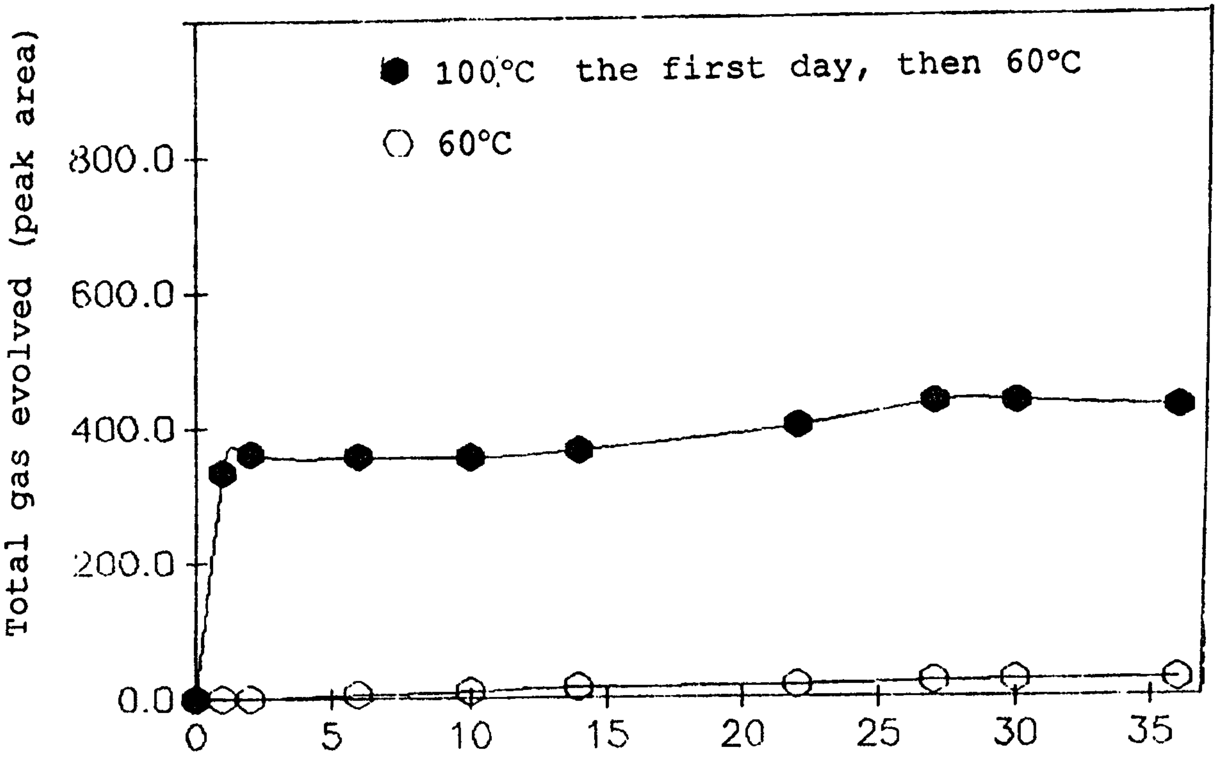

FIGURE 3
Autocatalytic effect of NO_2 on the decomposition of TMETN.

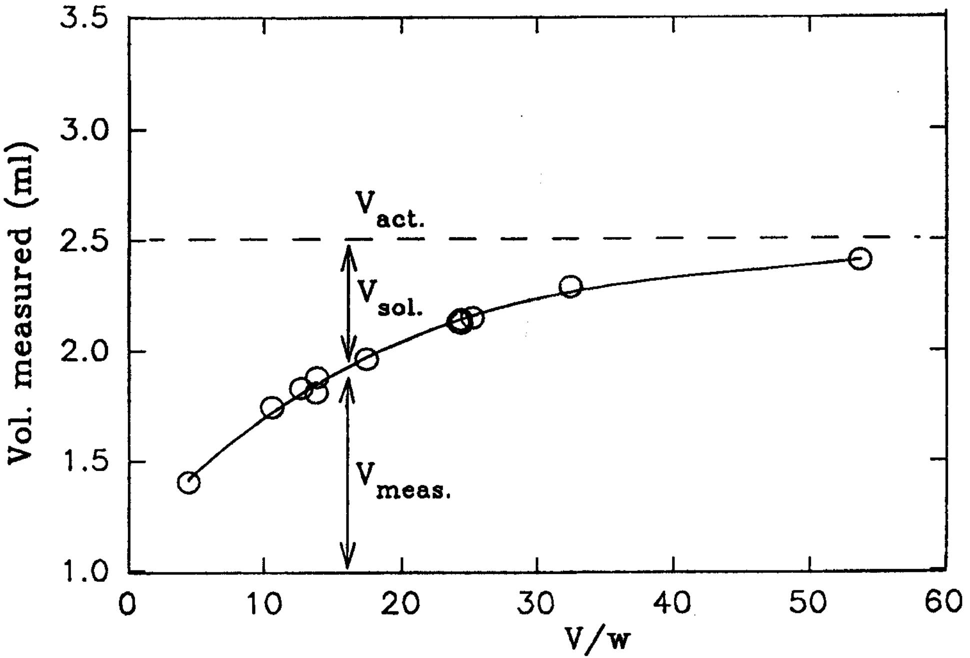

FIGURE 4
Effect of solubility on the volume measured for AN/BDNPAF mixture at 100°C for 48 hours.
Actual volume (V_{act}) = volume measured ($V_{meas.}$) + volume due to solubility ($V_{sol.}$).

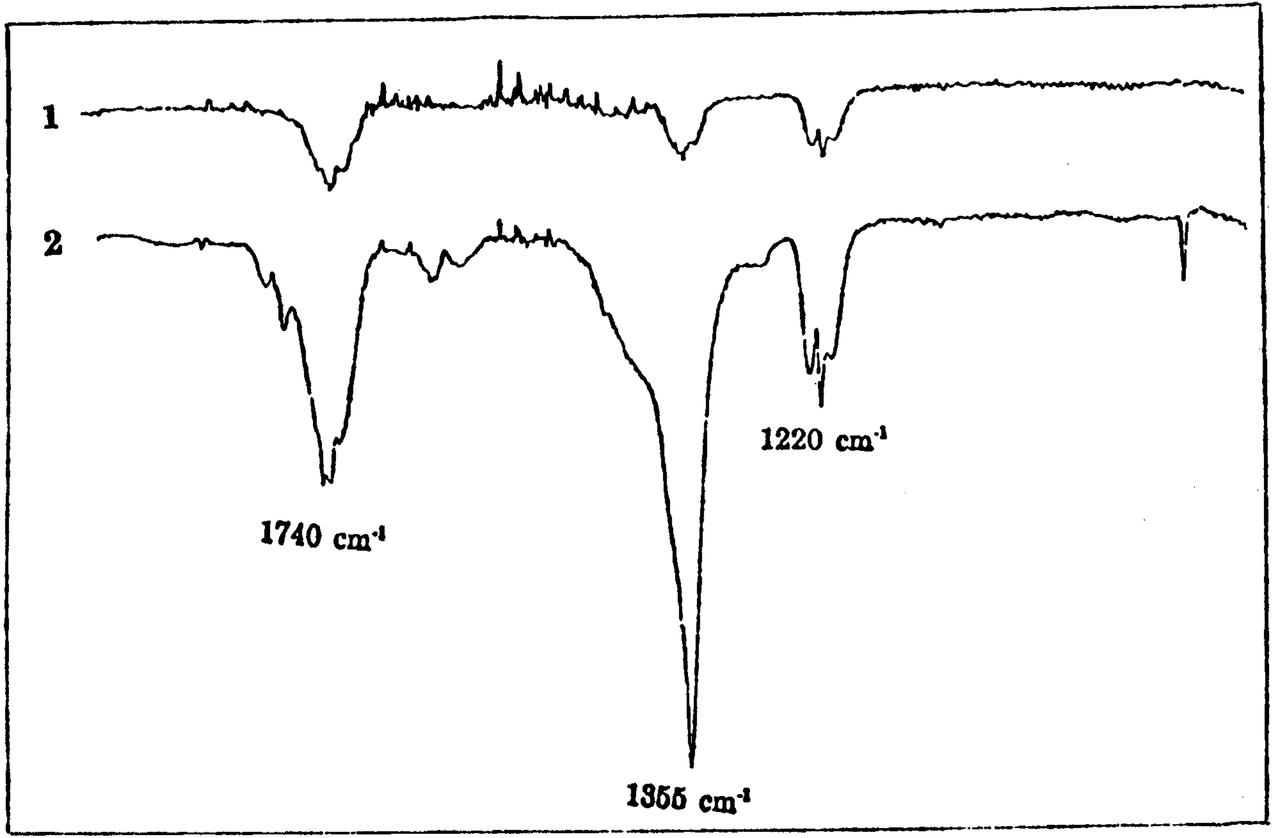

FIGURE 5
Infra-Red spectrum of evolved gas from BTTN.
1: after 1 hour at 20°C; 2: after 5 hours at 100°C.

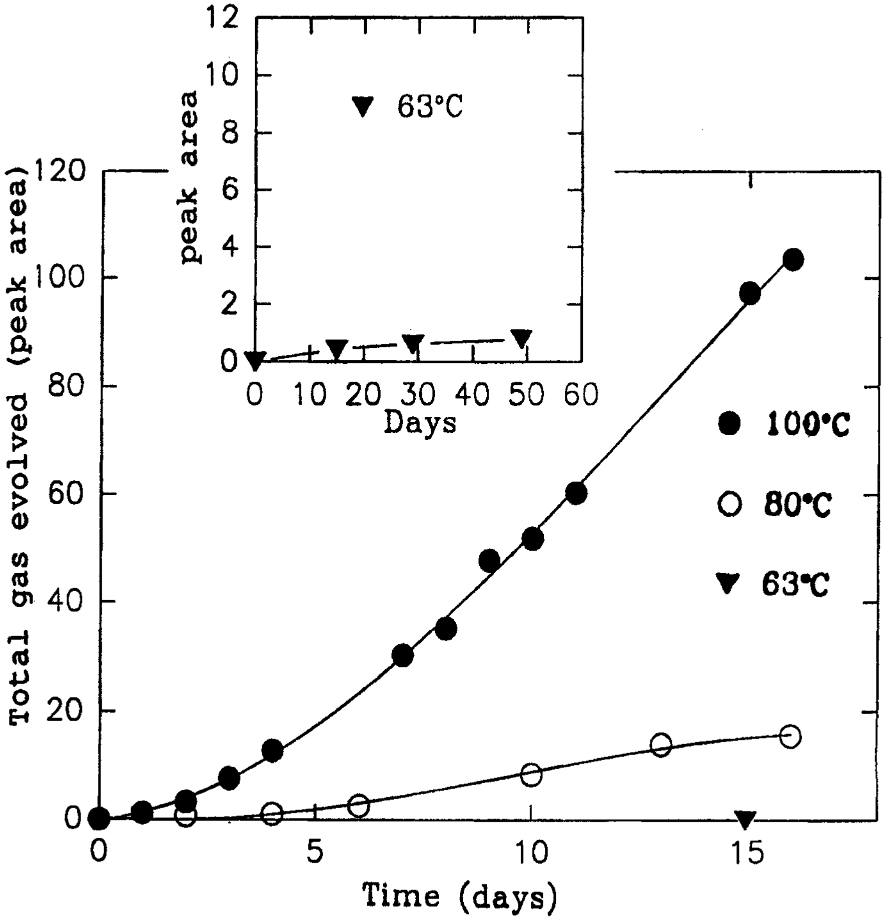

FIGURE 6
Gas evolution as a function of time (2g of TMETN).