

CONF-95/263--1
SAND 95-2724C

**CALIBRATION OF AN EXPLOSIVES VAPOR GENERATOR BASED ON
VAPOR DIFFUSION FROM A CONDENSED PHASE**

John E. Parmeter, Charles L. Rhykerd, Jr., and Frank J. Conrad, Department 5848,

Sandia National Laboratories, Albuquerque, NM, 87185-0782

Gregory S. Tiano, Douglas Preston, and Gary A. Eiceman, Department of Chemistry and

Biochemistry, New Mexico State University, Las Cruces, NM, 88003-8001

James T. Arnold, Ginzton Research Laboratory, Varian Associates, 3075 Hansen Way,

Palo Alto, CA, 94304

Development of a vapor generator for consistently producing accurate amounts of vapor from low vapor pressure explosive materials is a pressing need within the explosives detection community. Of particular importance for reproducibility and widespread acceptance of results is the correlation of such a vapor generator to a National Institute of Standards and Technology (NIST) mass standard. This paper describes an explosives vapor generator recently developed at Varian in which a solid explosive sample in a precision bore glass tube is put in an oven at constant temperature, and vapor diffusing from the top of the tube is entrained in a carrier gas flow. The rate of vapor output is thus dependent on both the equilibrium vapor pressure of the solid at oven temperature and the rate of diffusion up the length of the tube. Correlation to a NIST mass standard is

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED *et*

DISCLAIMER

**Portions of this document may be illegible
in electronic image products. Images are
produced from the best available original
document.**

achieved by periodic weighing of the sample tube on a microbalance. We report results obtained with the explosives TNT and RDX. Results for TNT show that the mass output rate is constant over hundreds of hours of continuous use, with outputs of ~ 10 -2000 pg/sec for oven temperatures in the range of 60-120 °C. Both the mass loss experiments and calibration with an ion mobility spectrometer (IMS) give a TNT mass output value of 85 pg/sec at 79 °C, and this result is supported by transport theory calculations. Mass loss curves for RDX are also linear with time, and show the expected exponential increase of mass output with oven temperature.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Introduction

The development of accurate vapor generators for low vapor pressure explosives is an area of active research within the explosives detection community. Various attempts have been made to develop vapor generators capable of operating in discrete, pulsed, and continuous flow modes. Discrete mode operation typically involves placing a known mass of explosive onto a surface, followed by heating the surface to desorb the explosive. Some highly accurate discrete generators have been developed recently [1]. Such generators are usually inexpensive and easy to operate. However, discrete generators are generally not capable of producing continuous, quantifiable vapor pulses for a desired length of time, and the amount of material vaporized must be known (i.e. carefully measured out) prior to evaporation. In some cases, loss of material due to decomposition of the explosive on the desorbing surface or poor spatial direction of the desorbing flux may also be a problem. For maximum flexibility in operation, a vapor generator that can produce a well-quantified vapor flux both continuously or in timed pulses is desirable. Ideally, the explosive mass output rate and the pulse time should be independently variable. In addition, tying the measured mass outputs to a National Institute of Standards and Technology mass standard is desirable to ensure accuracy and widespread acceptance of the results.

In this paper, we discuss the calibration of a vapor generator capable of operating in both continuous flow and pulsed modes. The explosives studied to date are 2,4,6-trinitrotoluene (TNT) and cyclonite (RDX). The vapor generator used was developed by

Varian Associates [2], and is based on the principle of vapor diffusion up a glass tube from a solid or liquid explosive sample contained in the bottom of the tube. Upon exiting the tube, explosive vapor is entrained in a carrier gas and swept out of the exit nozzle of the generator. The results obtained indicate that this generator can serve as a convenient, quantifiable source of explosives vapor, once an initial time investment for calibration experiments has been made.

Description of the Varian Vapor Generator

Figure 1 shows a photo of the Varian vapor generator interfaced to an ion mobility spectrometer. A schematic diagram of the inside of the generator is shown in Figure 2. The overall system consists of the generator and its housing, a control box for setting and monitoring the carrier gas flow rate and the various temperatures within the generator, and a hand-held switch box. The switch box controls a solenoid valve that allows the carrier gas/explosive vapor to be directed either through the generator exit nozzle, or out a separate line at the bottom of the generator. When the generator is interfaced to a detector, flow out the exit nozzle corresponds to the "on" position, while flow out the bottom of the generator corresponds to the "off" position. If flow out the bottom of the generator is likely to lead to environmental contamination problems, this can in principle be remedied by connecting either a zeolite trap (to remove explosive vapor from the flow) or a long hose (to direct the flow out of test area) to the line at the bottom of the generator.

The operation of the vapor generator is straightforward. A small amount of solid explosive is placed in a glass tube, which is in turn placed in the sample oven of the generator. A glass stopper seals the opening where the glass tube is placed in the instrument, and the control box is used to set appropriate temperatures and carrier gas flow rate. Four parts of the generator have independent temperature control: the sample oven; the carrier gas preheating oven; the mixing chamber, where the entering carrier gas meets explosives vapor diffusing from the glass tube; and the exit nozzle. Typically, the sample oven and carrier gas preheating oven are set at the same temperature, the mixing chamber is set about 2 °C hotter, and the nozzle is set 5 °C hotter than the mixing chamber. The carrier gas is typically nitrogen or purified air contained in a standard compressed gas cylinder, and is run at a rate on the order of 100-200 cubic centimeters per minute (cc/min).

Under these conditions, the flux of explosives vapor out the nozzle of the generator is controlled by the sample oven temperature and by the dimensions (length and inner diameter) of the glass tube containing the sample. There may also be a slight dependence on atmospheric pressure due to the pressure dependence of the gas phase diffusion coefficient (see next paragraph). Provided that the system has been allowed to come to equilibrium, the amount of solid explosive present in the sample tube is not important as long as some is always present and as long as the amount present is small enough that the distance from the surface of the solid explosive to the top of the tube can be taken as constant while the material slowly evaporates. In other words, the fraction of the tube length occupied by the explosive sample should be small, probably less than 5% of the total

length. The choice of carrier gas also makes no difference provided that no decomposition of the explosives vapor occurs. For this reason relatively inert carrier gases are preferred. The carrier gas flow rate also does not affect the amount of explosives vapor produced per unit time. It does affect the concentration of the explosive within the carrier gas, which is cut in half if the carrier gas flow rate is doubled. Adsorptive losses of explosive on the inside walls of the tubing leading to the exit nozzle are unimportant once equilibrium has been reached in system operation, since by definition the rate of adsorption onto the walls will then equal the rate of desorption from the walls. In practice, 1-2 hours of operation at a chosen temperature appears to be more than adequate for reaching equilibrium with TNT. For RDX, the time is somewhat longer, and running the generator overnight before attempting quantitative work is advisable.

Under the above conditions, the flux (mass per unit time) of explosives vapor leaving the diffusion tube (and the exit nozzle) is predicted by transport theory to be

$$(1) \text{ output} = DAn_0/L,$$

where D is the gas phase diffusion coefficient of the explosive molecule, A is the cross sectional area of the tube opening, n_0 is the equilibrium vapor concentration (mass per unit volume) of the explosive at the sample oven temperature, and L is the tube length [2]. The diffusion coefficient D has units of cm^2/sec and is expected to be proportional to $T^{3/2}$ (where T is temperature in Kelvins) and inversely proportional to the ambient pressure [3].

~ D cannot be calculated exactly, and calculation of a generator output from equation (1) is

therefore not straightforward. However, a value of D in the range of 0.05 to 0.1 cm^2/sec is expected for a molecule such as TNT based on comparison to other molecules of similar size [4]. The main temperature dependence of the output will be in the n_0 factor, and since this quantity is expected to increase exponentially with oven temperature, the generator output is expected to do the same. Furthermore, it can be noted that the sample tube dimensions are critical, since vapor diffusion up the tube determines the flux leaving the top. Doubling the length is expected to reduce the output by a factor of two, while doubling the radius should lead to an increase of a factor of four.

Experimental Procedures

Two types of experiments were performed with the Varian vapor generator. At New Mexico State University (NMSU), continuous flow experiments were performed in which the vapor generator was run for hundreds of hours with a fixed sample oven temperature, and sample mass loss was monitored in order to calibrate the generator mass output. The glass tube containing the explosive sample was periodically removed from the generator and weighed on a Perkin-Elmer AD-6 microbalance. This balance has a reported accuracy of ± 0.1 micrograms (μg). The balance was calibrated with a NIST standard mass during each weighing procedure, and hence the results reported here are tied directly to this NIST standard. Nitrogen was used as the carrier gas at a flow rate of 100 cc/min. The glass tubes used to hold the explosives samples were 10 cm long with an inner diameter of 0.47 mm.

Work performed at Sandia National Laboratories (SNL) involved testing of the vapor generator in a pulsed mode. In these experiments, the generator output was directed into an ion mobility spectrometer (IMS) for time intervals ranging from 5-120 seconds. This pulsing was accomplished by manually operating the generator switch box. The carrier gas was air, at a flow rate of 175 cc/min, and the glass sample tubes were identical to those used at NMSU. For a given explosive and oven temperature, vapor pulses of different time duration were performed and the resulting signals on the IMS were integrated using a Spectra-Physics ChromJet integrator. These data yield a linear curve of vapor output (in arbitrary units) versus pulse time. To calibrate these data, a second IMS response curve was obtained using identical IMS conditions [5] for known amounts of explosive from standard explosives solutions. This was accomplished by using a syringe to place a measured amount of solution onto a 1/8" o.d. pyrex probe, allowing the solvent (acetonitrile) to evaporate, and then placing the probe directly into the IMS inlet. The inlet is maintained at an elevated temperature, and the explosive is quickly evaporated into the IMS, with the signal intensity again being measured with the Spectra-Physics integrator. This was done with different amounts of explosive ranging from 0.1-1.0 ng, resulting in a linear plot of mass vs. signal intensity. The slope of this line could then be used to provide an absolute calibration of the IMS signal vs. pulse time data obtained with the vapor generator. Taken together, these measurements provide a quantification of the generator output completely independent of that obtained in the continuous flow mass loss experiments. In addition, pulsing into the IMS allows the purity of the explosive vapor exiting the generator to be verified.

The explosives samples used in these studies were obtained from Pantex by SNL. Purity analysis of the TNT and RDX was performed at NMSU [6]. Using gas chromatography, the TNT was shown to be > 99.9% pure. Using liquid chromatography, the RDX was shown to be > 95% pure. The latter is a very conservative estimate and the purity is probably substantially higher, but further quantification was not possible with the test equipment available.

Results and Discussion

TNT

Figures 3, 4, and 5 show mass loss data as a function of time for TNT with generator sample oven temperatures of 79, 99, and 120 °C, respectively. Table I summarizes the output values calculated from these curves. Table I also lists an estimated output based on much cruder mass loss data obtained at 60 °C and measurements for pulsed mode operation obtained at 60 and 79 °C. The curves obtained at the three temperatures shown are very linear, with R^2 (correlation coefficient) values greater than 0.99. In addition, all three curves come very close to passing through the origin. This behavior is anticipated since by definition the mass loss should be zero for time $t = 0$. Figure 6 shows a plot of vapor generator output vs. temperature with the output plotted on a logarithmic scale. This plot approximates a straight line, showing that the mass output increases exponentially with temperature, as expected. In addition, combining the measured output

with equation (1) yields an estimate of the diffusion coefficient. For example, at 79 °C, the output is 85 pg/sec, A/L is 0.0173 cm based on the tube dimensions stated earlier, and tabulated vapor pressure data give an n_0 value of 63.8 ng/cm³ [7]. These numbers give an estimated D value of 0.078, which falls into the expected range. All of these results indicate that in the case of TNT the vapor generator functions reliably and in accord with theoretical predictions.

Results obtained with pulsed mode testing are shown in Figures 7 and 8. Figure 7 shows the integrated IMS signals for different pulsing times with a sample temperature of 79 °C. Results are plotted for three measurements each for pulses at 5-second time intervals ranging from 0 (background) to 30 seconds. The curve is linear with R^2 again greater than 0.99. All points fall on the line within the limits of experimental error, except for those for a 5-second pulse time. These are consistently low. This results from switching the carrier gas/explosive vapor flow path: due to the design of the generator, the carrier gas pulsed out the nozzle in the first 1-2 seconds after flow switching contains little explosives vapor. This leads to a large error for 5-second pulses, while for pulses longer than 10 seconds the error becomes negligible.

Figure 8 shows the IMS calibration curve obtained with TNT solution standard samples; the IMS conditions are identical to those employed for Figure 7. Four different data points were obtained for each of 10 different masses of TNT between 0.1 and 1.0 ng. This curve is also linear with $R^2 > 0.98$. Combining the slope of this line with the data in Figure 7, the pulsed mode output of the vapor generator is estimated to be 85 ± 5 pg/sec.

This precise agreement with the continuous flow mass loss experiments, obtained by a completely independent method, confirms the excellent performance of the generator under these conditions.

It was not possible to perform pulsed mode calibration at 99 and 120 °C because the TNT output at those temperatures is high enough to saturate the IMS. Thus, the output would be above the linearity range of the instrument [8], and any attempt to estimate the output by calibration against solution standards would result in an underestimate of the output. However, the results obtained at these temperatures in the mass loss measurements are believed to be just as accurate as those obtained at 79 °C. This is because the R^2 values for linear fits to the data are similar, and because the accuracy of the mass loss experiments increases at higher temperatures as the mass loss per unit time increases. Pulsed flow data obtained for a sample oven temperature of 60 °C yield a mass output of 13 pg/sec, which at this low temperature is probably more accurate than the mass loss estimate of ~ 17 pg/sec.

Pulsed flow data also confirm that the output of the generator is pure TNT entrained within the carrier gas flow, and that decomposition and contamination by impurities are negligible. Figure 9 shows three ion mobility spectra. Spectrum (a) is the background spectrum that results when no TNT is directed into the IMS; this can be thought of as the spectrum of ambient air along with the methylene chloride carrier gas. The large reactant ion peak, which is deliberately shown off scale so that smaller peaks can be observed easily, corresponds to Cl^- . The remaining two small peaks at low retention time appear to

be associated with vapors emanating from humans present in the room (e.g., pyruvic acid). Spectrum (c) results when TNT from the generator with a sample oven temperature of 79 °C is pulsed into the IMS. The peak in the right hand window (at a retention time of 12.05 ms) is characteristic of TNT, and it can be seen that no additional impurity or decomposition peaks are observed. This is true for sample oven temperatures up to at least 120 °C. Spectrum (b) shows the response of the IMS when a bottle containing solid 2,4-dinitrotoluene is held up to the inlet flow. The signature peak of DNT appears in the left hand window at 11.4 ms, and it is clear that no such peak is present in the TNT output shown in spectrum (c). This is of particular importance because it has been suggested that DNT impurities in TNT may contribute to erroneous vapor generation measurements. The purity of the TNT output as judged from these IMS spectra is consistent with the estimate of > 99.9% purity obtained from GC studies [6].

RDX

Mass loss measurements similar to those performed with TNT were also performed with RDX, and the results are summarized in Table II. The values given for 110 and 129 °C are averages for two different experimental runs. Data for these two temperatures are plotted in Figures 10 and 11. It can be seen in Figure 11 that the two curves obtained at 129 °C are very linear ($R^2 > 0.98$), but the output values differ by ~ 20%. Thus the output under these conditions should probably be taken to be 270 ± 50 pg/sec. Figure 10 shows that the data obtained at 110°C are less linear ($R^2 \sim 0.90$), and the output obtained from

chart A is nearly 50% greater than that obtained from chart B. Furthermore, both curves have a y-intercept that is offset considerably from the ideal value of zero, suggesting an initial period of substantially more rapid mass output. This could result from volatile impurities being "baked out" of the RDX, or from the evaporation of RDX particles that are stuck to the inner walls of the sample tube well above the bottom of the tube following RDX sample introduction. Whatever the cause, these data indicate that running the generator overnight is advisable before attempting quantitative experiments with RDX. Clearly, the mass output at 110 °C is sufficiently low that the accuracy of the mass loss measurements becomes substantially reduced, and quantitative experiments would best be run using sample oven temperatures at or above 129 °C.

It was not possible to obtain a reliable measurement of the vapor generator output in pulsed flow mode using an IMS, as was done in the case of TNT. First, RDX generally gives rise to two rather than one peak in the IMS spectrum, and the variations in intensity of the two peaks appear to depend on the manner and speed of the RDX injection into the IMS. This is true not only of RDX produced by the vapor generator, but for vapor from solid RDX in a bottle and RDX from standard solutions as well, and in some cases a weak third peak (less than 10% of total integrated area) is also present. Any attempt to integrate two or three peaks would involve the assumption that the IMS is equally sensitive to the RDX in the forms corresponding to each peak, which is not necessarily true. Second, the mass calibration curves obtained with standard solutions of RDX (integrating all peaks) tended to be somewhat quadratic rather than linear, rendering the determination of a "slope" subject to considerable errors. Nevertheless, attempts were

made to measure the mass output at 110 °C by this method, and values were obtained in the range of 24-85 pg/sec. Thus it can be said only that the estimates obtained agree with the mass loss measurements to within a factor of two. No IMS peaks were observed in these experiments that could not be attributed to RDX.

From a theoretical perspective, the output rates measured for RDX are not as well understood as those obtained for TNT. While the mass output values obtained at 129 and 150 °C are believed to be accurate to within $\pm 20\%$, plugging the values into equation (1) to back out values for D yields values close to 1.0 rather than 0.1 cm²/sec.. Since this seems unreasonably high, it is concluded that the gas phase diffusion model used to obtain equation (1) probably does not fully describe the functioning of the generator for this very low vapor pressure molecule. It is possible that diffusion of RDX up the sides of the inside walls of the sample tube may occur to a significant degree, thus increasing the measured output. Since RDX has approximately 1/1000 the vapor pressure of TNT, it is also possible that the tabulated vapor pressure data for RDX (used to estimate D) are considerably less accurate. It is worth noting that the RDX data do show the expected exponential increase in output with sample temperature, and we thus believe that the results must be related to real physical effects.

Conclusions

An explosives vapor generator based on diffusion of vapor from a condensed phase contained in a glass sample tube has been tested for generation of TNT and RDX vapor.

In the case of TNT, the mass output is stable over hundreds of hours, and has been measured at three different temperatures via sample mass loss experiments. At one temperature (79 °C), the mass output has been confirmed by performing an independent calibration using ion mobility spectrometry. The mass outputs are also in agreement with transport theory predictions concerning the functioning of the generator. The output values measured at 79, 99, and 120 °C are believed to be accurate to within $\pm 10\%$, and are in the range of 85-2000 pg/sec. These outputs have been tied directly to an NIST mass standard. While these numbers were obtained primarily by performing experiments in a continuous flow mass loss mode, they are valid for pulsed mode operation as long as the pulses used are not shorter than 10-15 seconds. The output values obtained should be reproducible in any laboratory provided that the same sample oven temperature and sample tube dimensions are used. The only possible minor change anticipated is that the output values might be slightly lower at sea level ($p = 760$ Torr) than at SNL ($p \sim 620$ Torr) and NMSU ($p \sim 670$ Torr) due to the expected $1/p$ dependence of the gas phase diffusion coefficient.

In the case of RDX, mass loss calibration of the output has also been performed at three different temperatures. The values obtained at 129 and 150 °C, which are approximately 270 and 2000 pg/sec, are believed to be accurate to within $\pm 20\%$. In contrast to TNT, the results are not in full agreement with simple gas phase transport theory, and more work is needed to understand the functioning of the generator with this molecule.

Some further experimentation with this generator is desirable before it is introduced into widespread use. The most pressing needs are (1) more detailed studies with RDX and other explosives such as PETN, and (2) calibration experiments with TNT performed at sea level, to determine the degree to which the change in atmospheric pressure influences the mass output.

Acknowledgments

Others at Sandia who have contributed to this work include Brady Pompei, James Chapek, Chad Custer, David Hannum, and Christian Lastoskie. This work was funded in part by the United States Department of Energy under contract DE-AC04-94AL-85000. Primary funding for this research came from the Department of Energy Office of Safeguards and Securities, and from the Federal Aviation Administration under interagency agreement number DTFA03-95-X-90005.

References and Notes

- [1] For example, see C. S. Giam, progress report to the Federal Aviation Administration on award no. 93-G-0025 (1995).
- [2] More detailed information concerning the vapor generator, as well as a derivation of equation (1), is included in the vapor generator manual written by James Arnold. A copy may be obtained from Varian Associates, 3075 Hansen Way, Palo Alto, CA, 94304.
- [3] P. W. Atkins in Physical Chemistry, W. H. Freeman and Company, San Francisco, 1978. The relevant equation is given on p. 809.
- [4] This statement is based on data for similar and smaller molecules. See, for example, CRC Handbook of Chemistry and Physics, 56th edition, 1975, p. F-60.
- [5] The IMS used in these studies was a PCP-100. The IMS inlet and housing temperatures were set at 147 °C for TNT and 200 °C for RDX. In all cases, the high voltage was set at 3 kV and methylene chloride was used as the carrier gas.
- [6] G. S. Tiano and G. A. Eiceman, unpublished data.
- [7] B. C. Dionne, D. P. Rounbehler, E. K. Achter, J. R. Hobbs, and D. H. Fine, *Journal of Energetic Materials* 4, 447 (1986).
- [8] An ion mobility spectrometer typically has two orders of magnitude in sample mass over which the instrument's response is linear, and for higher doses instrumental saturation occurs. G. Eiceman and Z. Karpas, in Ion Mobility Spectrometry, CRC Press, Boca Raton, 1994, pp. 130-132.

Table I: Vapor generator output (pg/sec)
for TNT at different temperatures.

| Temperature (°C) | Mass Loss Measurement | IMS Measurement |
|---------------------|--------------------------|--------------------|
| 60 | ~17 | ~13 |
| 79 | 85 | 85 |
| 99 | 520 | — |
| 120 | 2000 | — |

Table II: Vapor generator output (pg/sec)
for RDX at different temperatures.

| Temperature (°C) | Mass Loss Measurement |
|------------------|-----------------------|
| 110 | 42 |
| 129 | 270 |
| 150 | 2000 |

Figure Captions

- (1) Photograph of the Varian vapor generator interfaced to an ion mobility spectrometer.
- (2) Schematic representation of the gas flows inside the Varian vapor generator.
- (3) Mass loss curve for TNT at 79 °C.
- (4) Mass loss curve for TNT at 99 °C.
- (5) Mass loss curve for TNT at 120 °C.
- (6) TNT vapor output vs. sample oven temperature.
- (7) Ion mobility spectrometer response to TNT vapor pulses of different time duration.
- (8) Calibration of the ion mobility spectrometer response to TNT using standard solutions.
- (9) Ion mobility spectra of (a) room air (background), (b) DNT from solid sample in a jar, and (c) TNT from the vapor generator at 79 °C.
- (10) Mass loss curves for RDX at 110 °C.
- (11) Mass loss curves for RDX at 129 °C.

Varian Vapor Generator Interfaced to an Ion Mobility Spectrometer

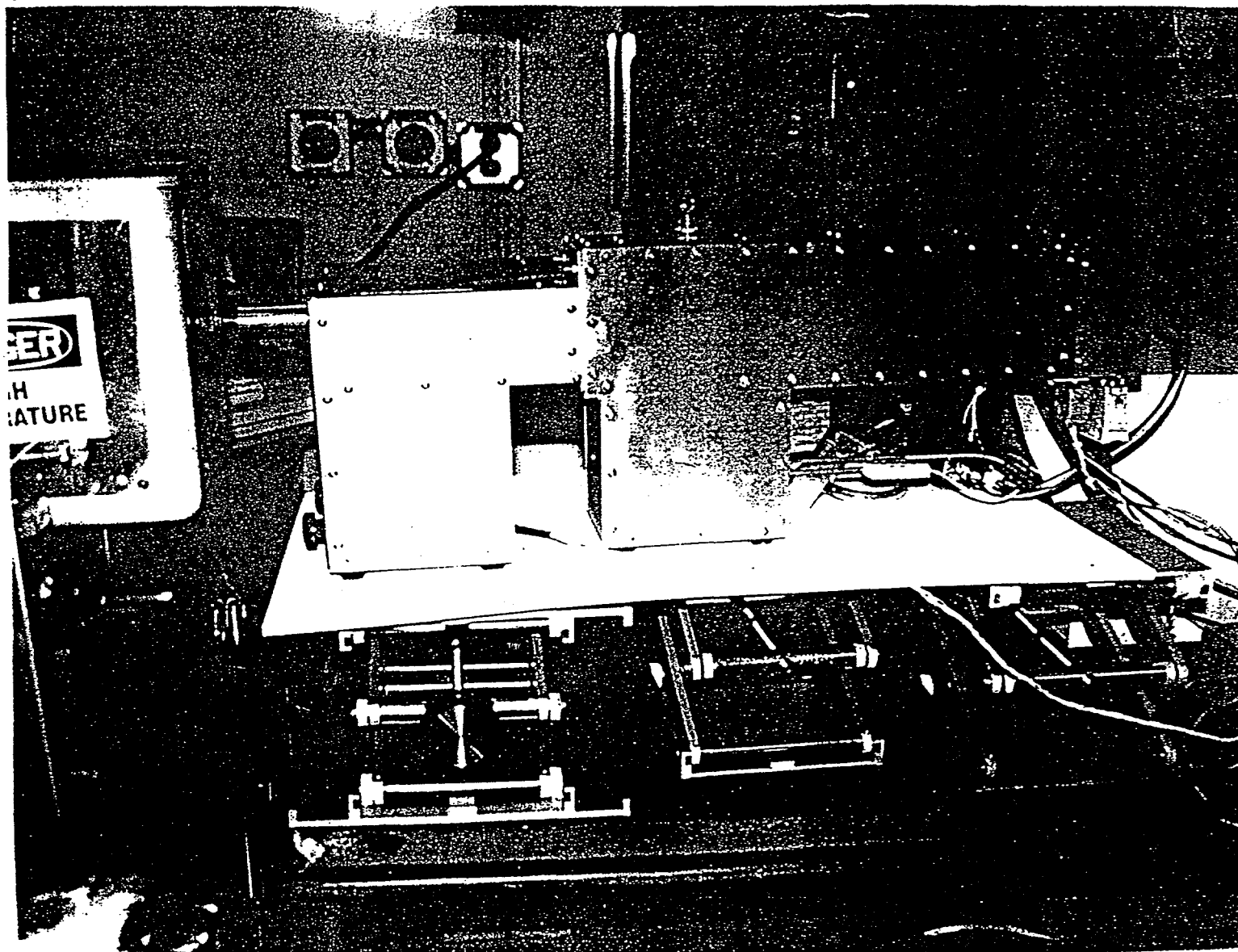
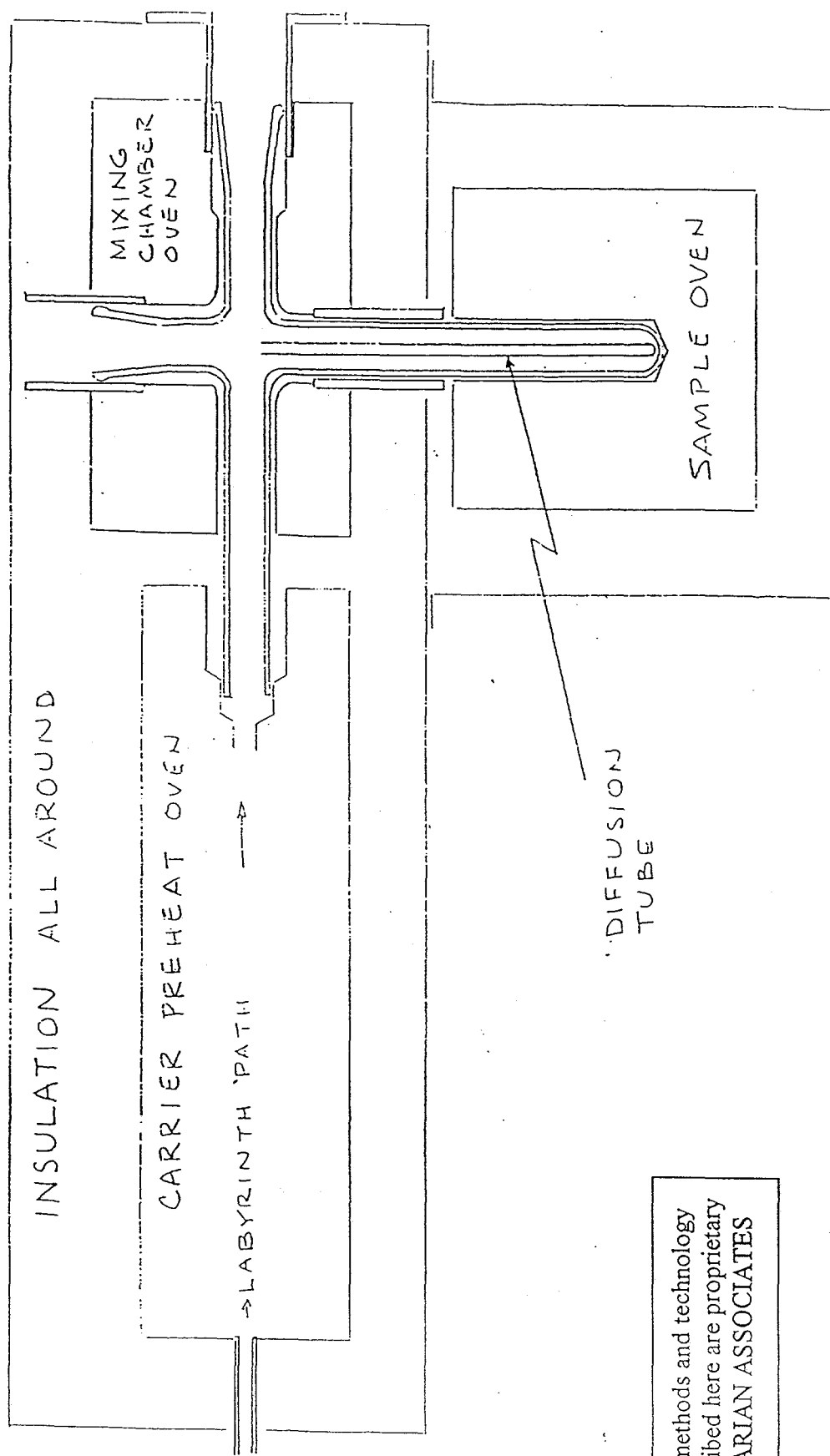


Figure 1



The methods and technology described here are proprietary to VARIAN ASSOCIATES

Figure 2

Vapor Generator Output for TNT at 79 C

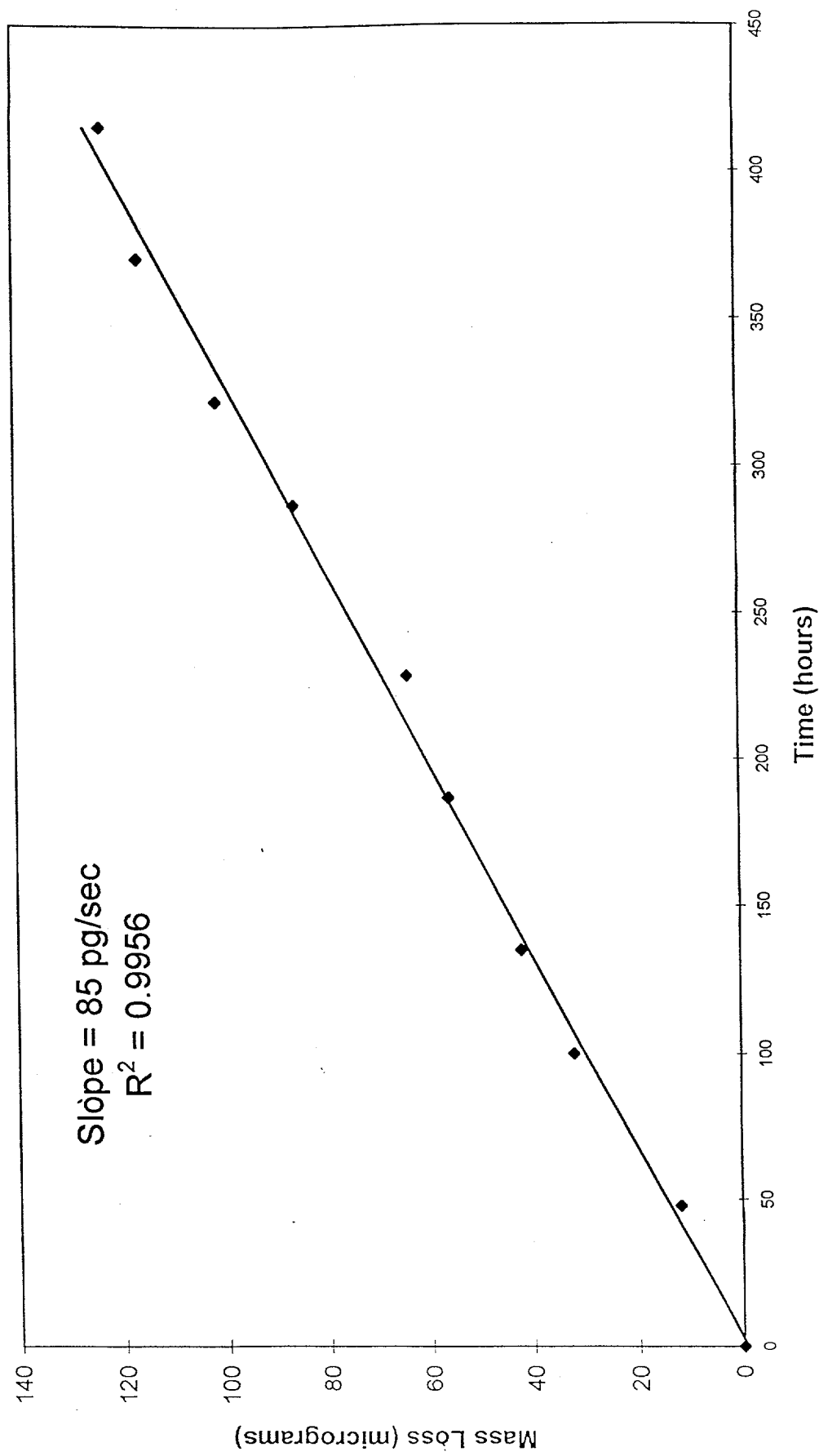


Figure 3

Vapor Generator Output for TNT at 99 C

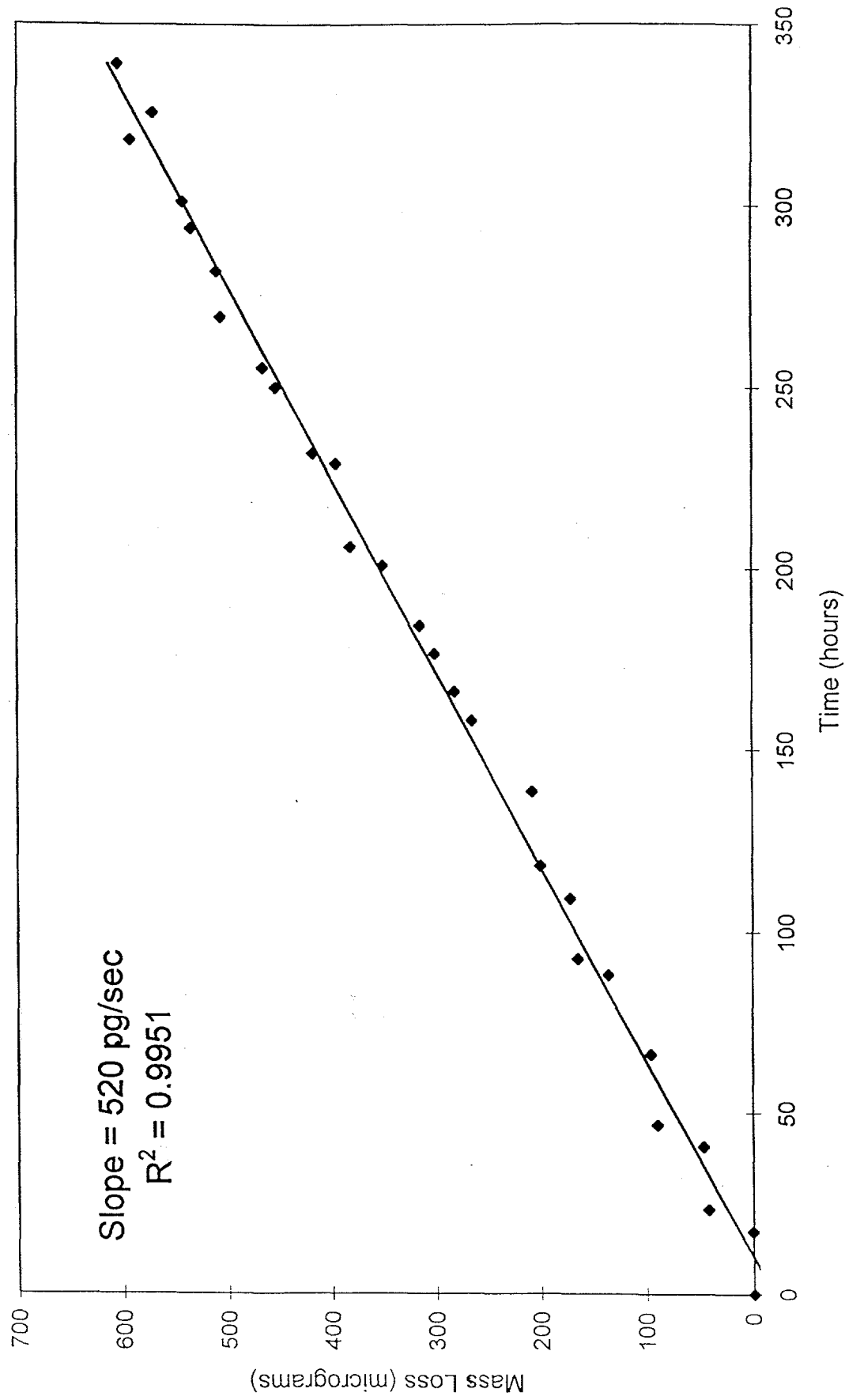


Figure 4

Vapor Generator Output for TNT at 120 C

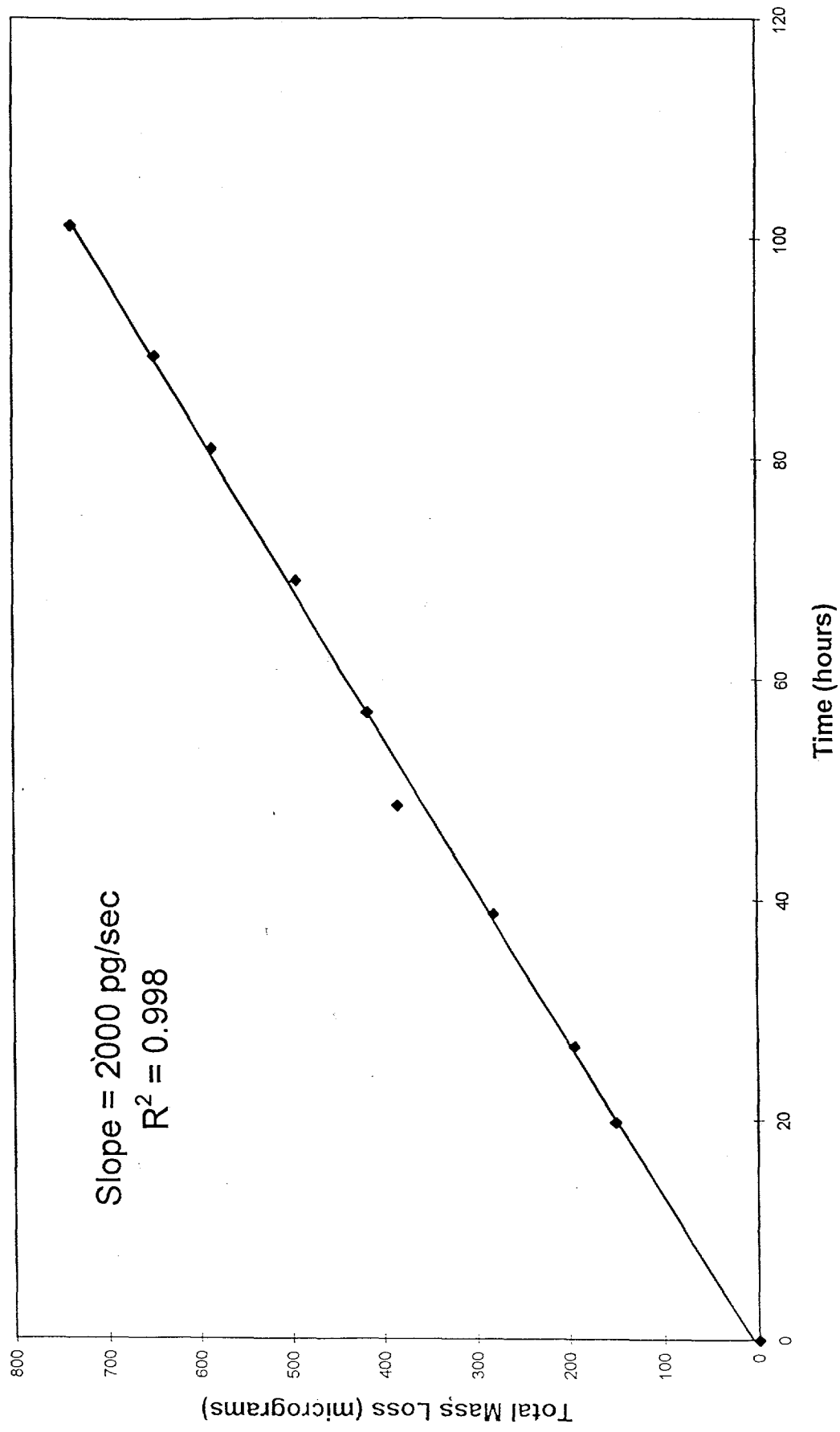


Figure 5

Vapor Generator Output for TNT as a Function of Temperature

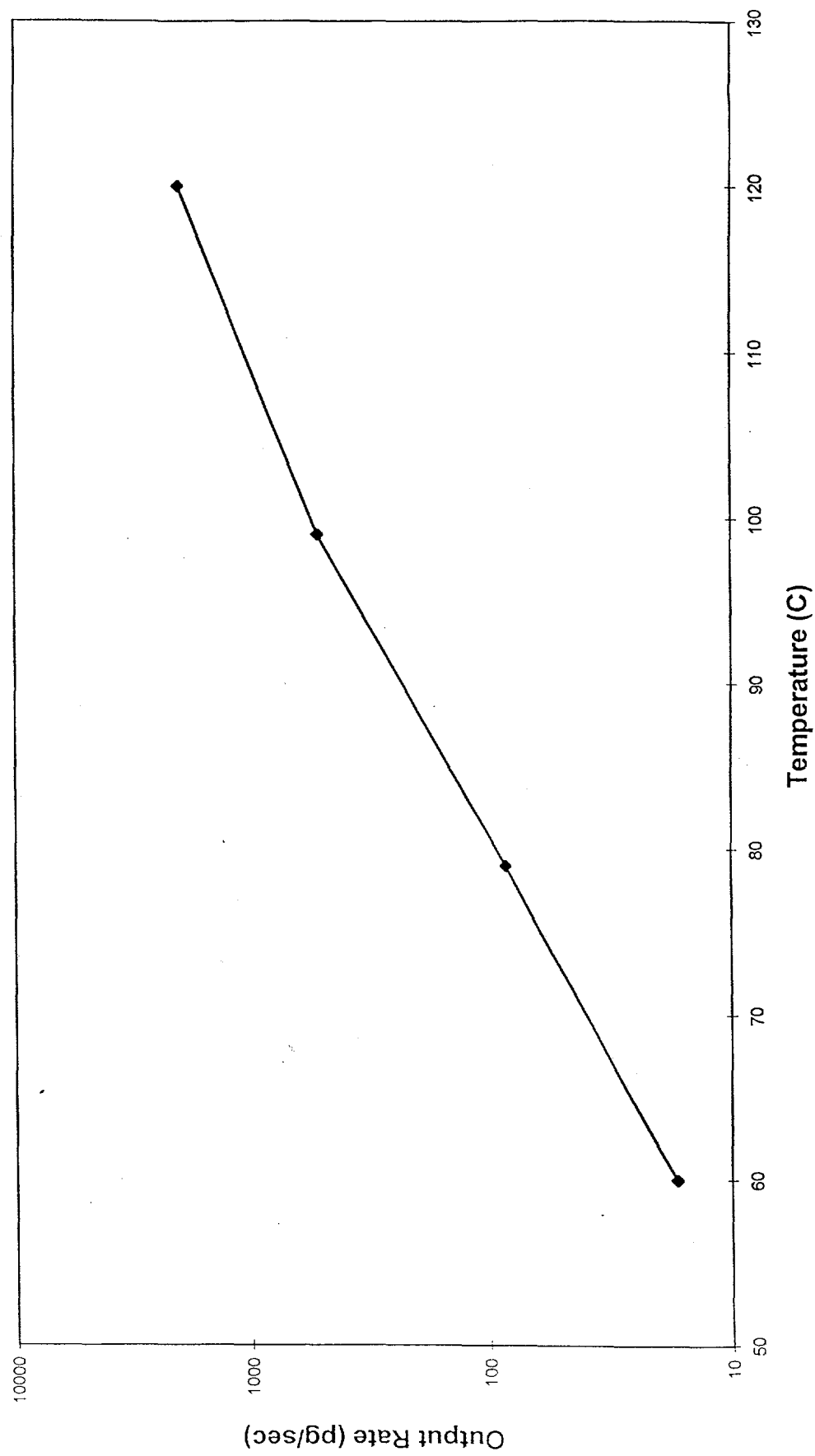


Figure 6

Vapor Generator Output for TNT at 79 C

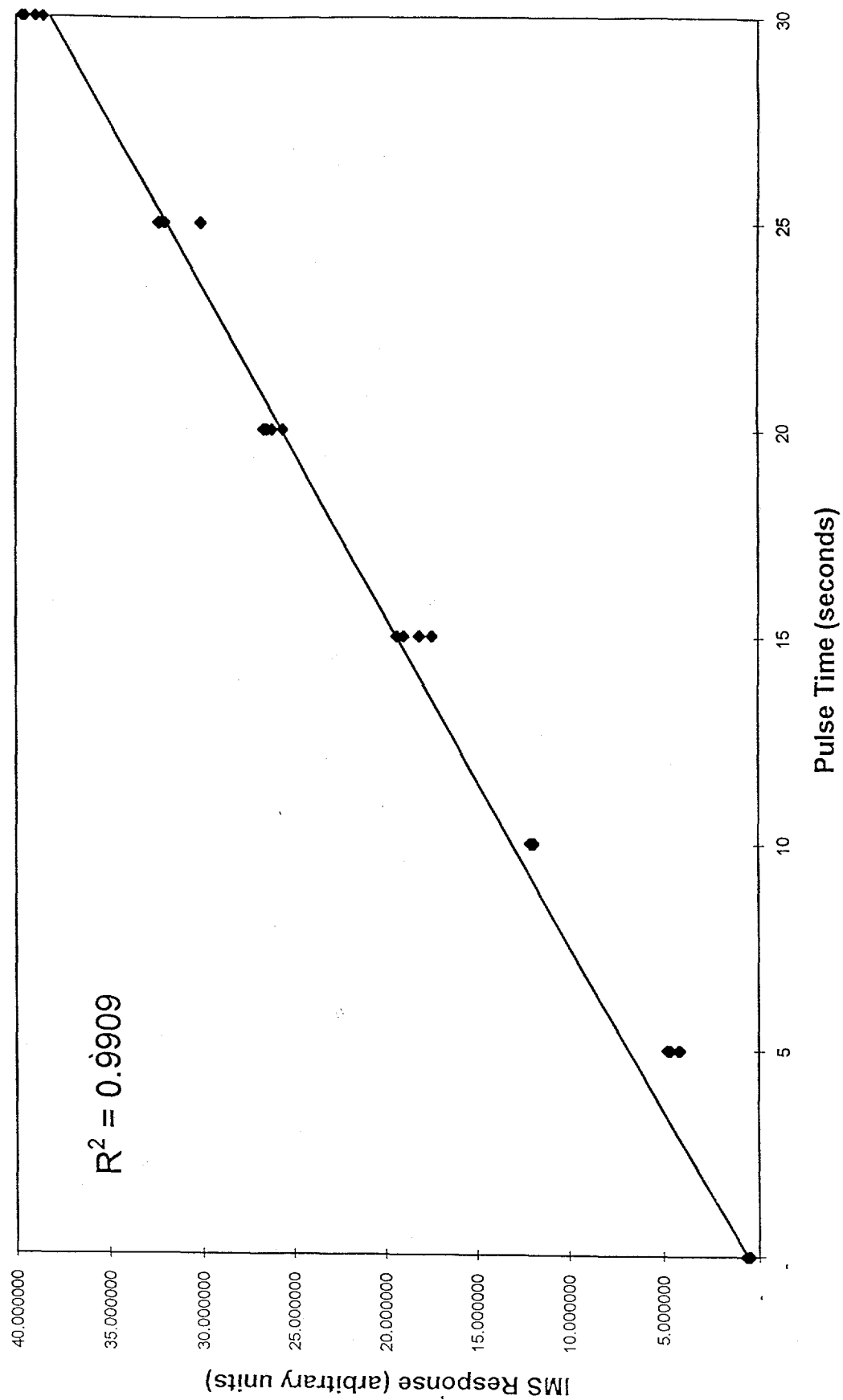


Figure 7

IMS Response to TNT Solution Standards

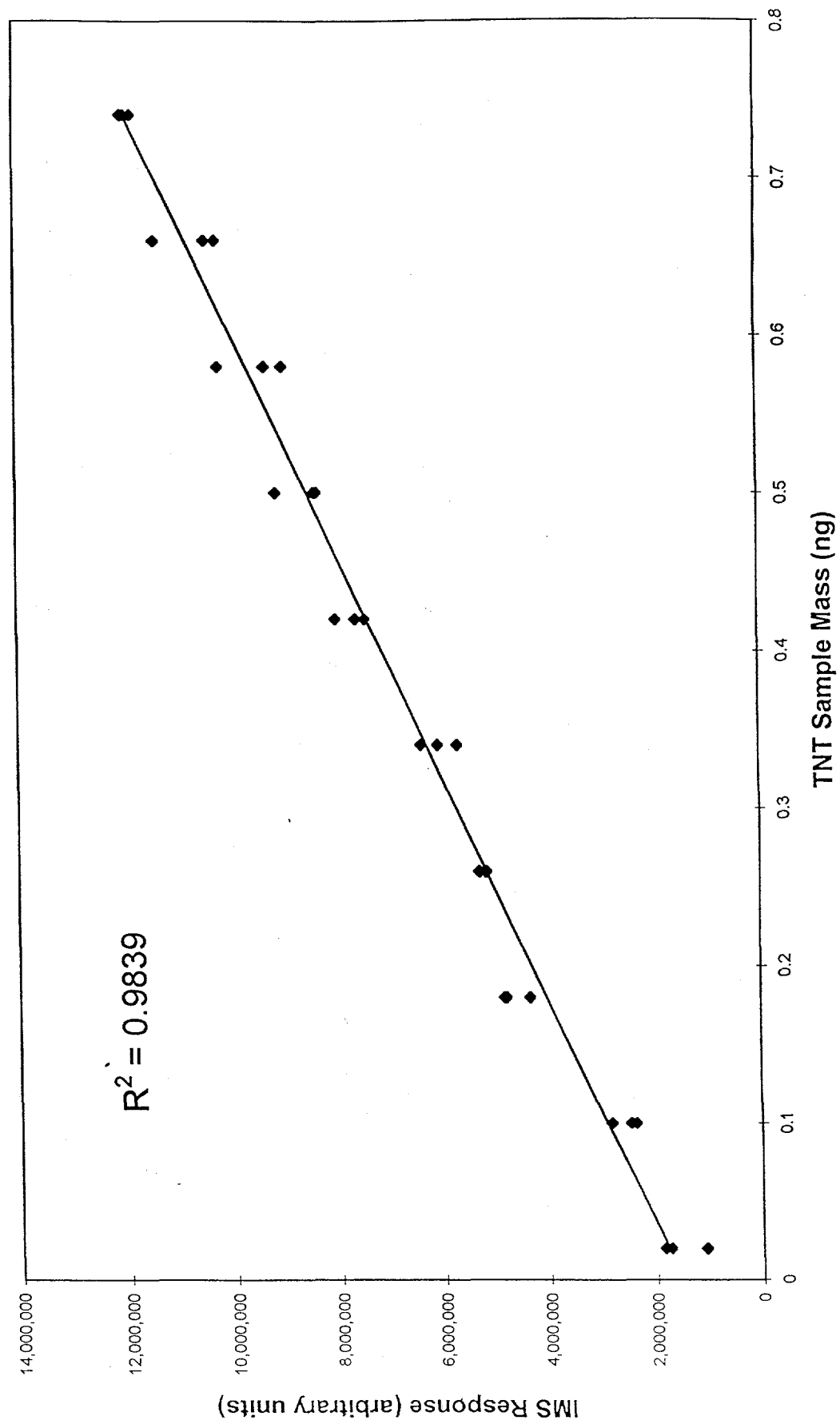


Figure 8

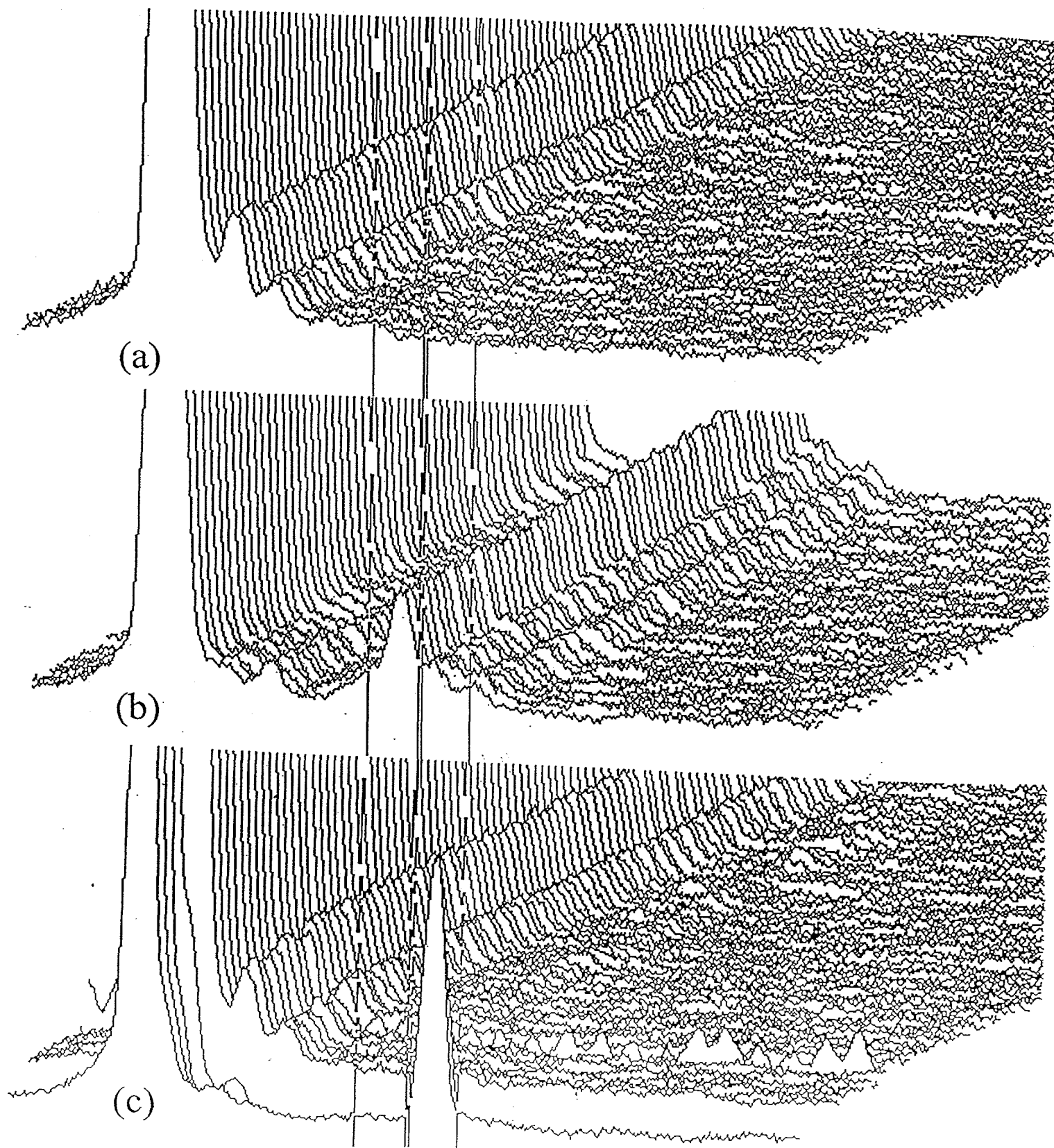


Figure 9

RDX Vapor Generation at 110 C

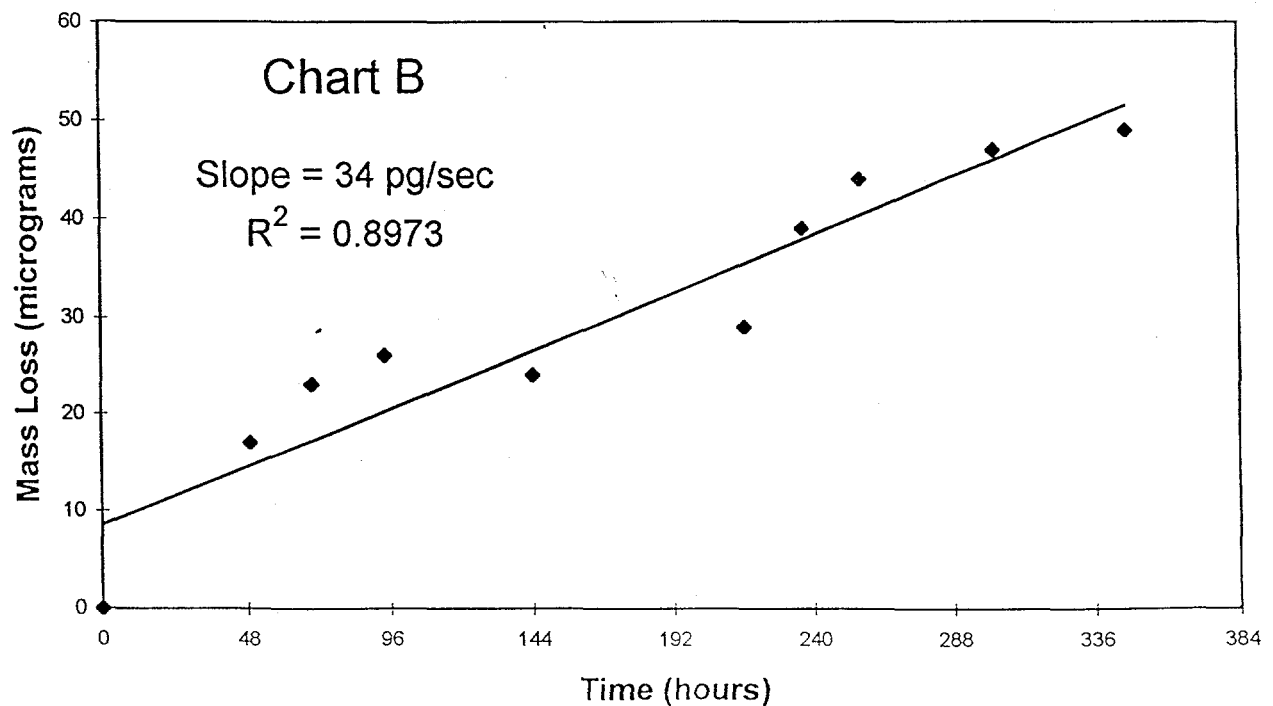
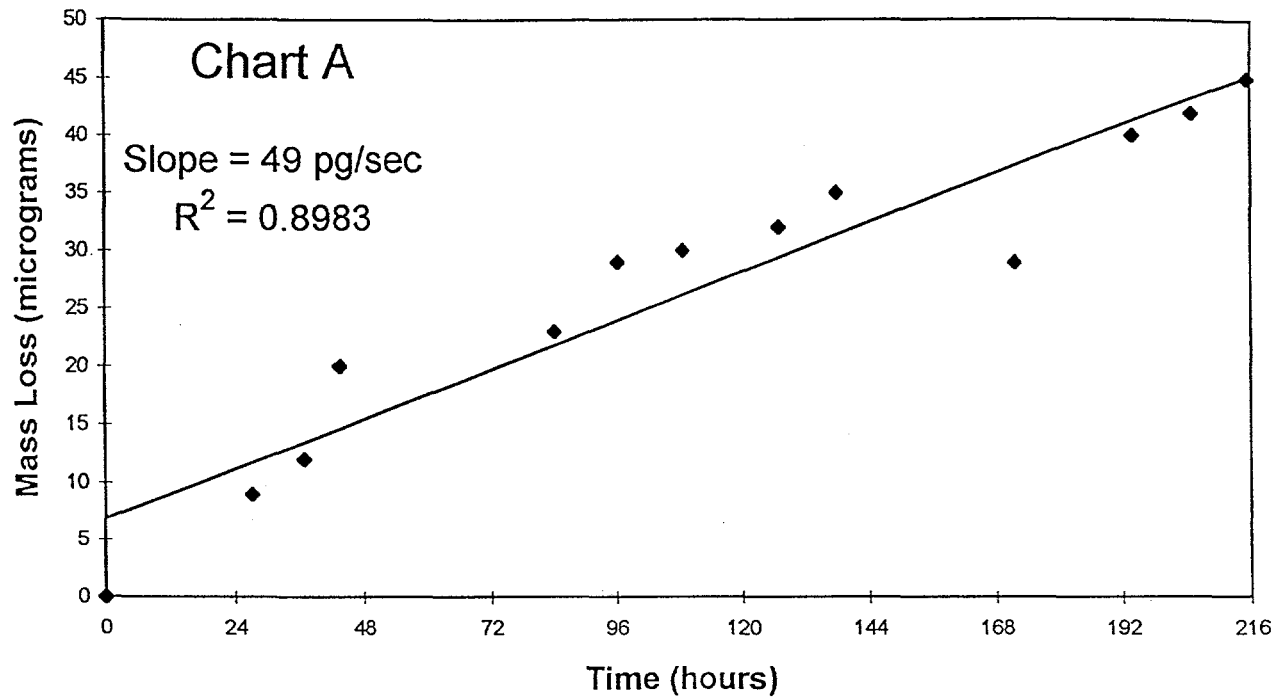


Figure 10

RDX Vapor Generation at 129 C

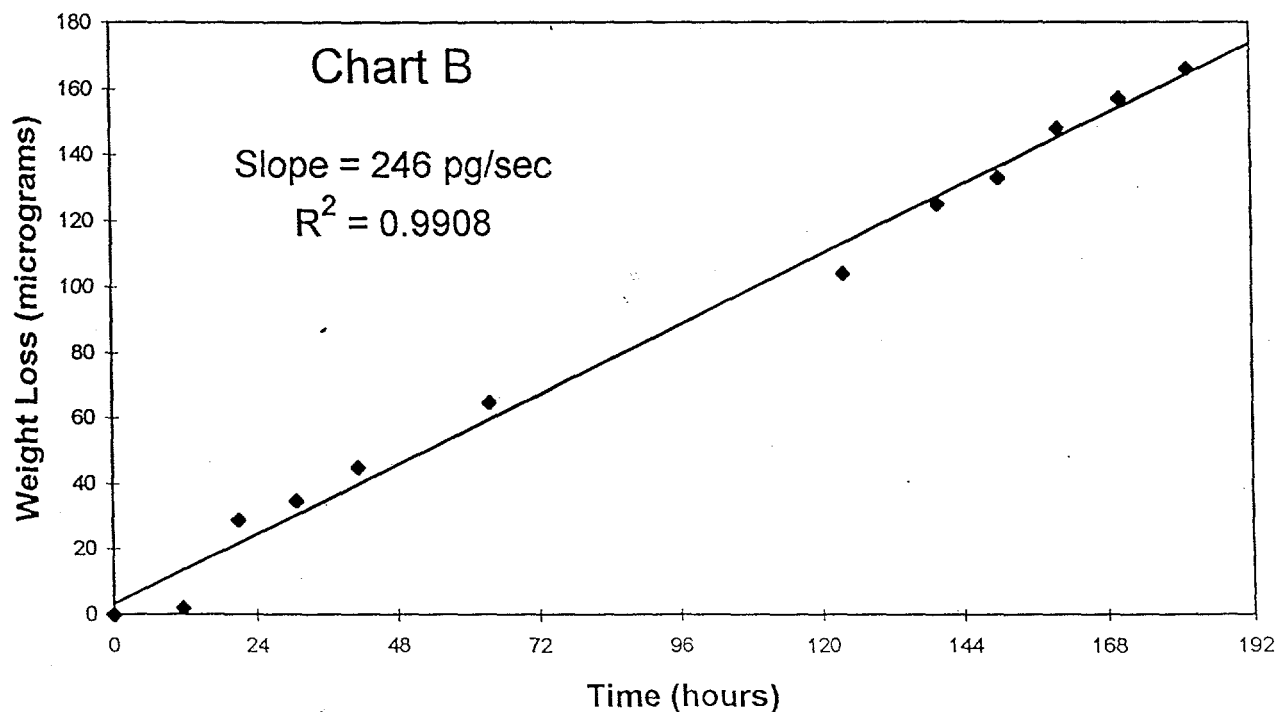
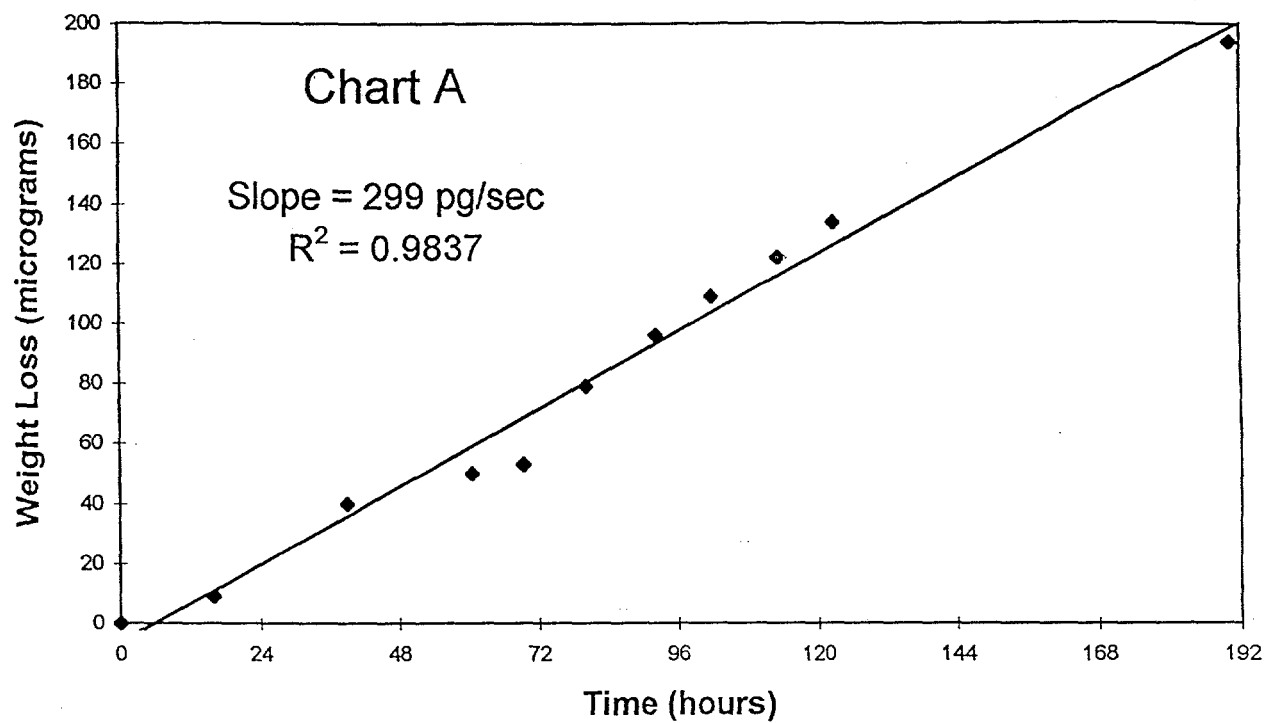


Figure 11