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PML 1992-A78

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Characterization of plastic bonded explosives by pyrolysis-gas chromatography and multivariate data analysis. Development of the procedure

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TDCK **RAPPORTENCENTRALE**
Frederikkazerne, gebouw 140
v/d Burchlaan 31 **MPC 16A**
TEL. : 070-3166394/6395
FAX. : (31) 070-3166202
Postbus 90701
2509 LS Den Haag

TD 92-2398

TNO Defence Research

TNO Prins Maurits Laboratory

La[illegible]
P.[illegible] **TD** 92-23988
2280 AA Rijswijk
The Netherlands

Fax +31 15 84 39 91
Telephone +31 15 84 28 42

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Characterization of plastic bonded explosives by pyrolysis-gas chromatography and multivariate data analysis. Development of the procedure

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Author(s):

M. Rietjens

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SAMENVATTING

Titel	: Karakterisering van kunststof gebonden explosieven met pyrolyse-gaschromatografie en multivariate data analyse. Ontwikkeling van de procedure
Auteur	: M. Rietjens
Datum	: oktober 1994
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De verdere ontwikkeling van de methode gebaseerd op pyrolyse- gaschromatografie (PY-GC) voor de karakterisering van kunststof gebonden explosieven (PBX'en) wordt beschreven. Na het malen werden de PBX-monsters op een pyrolyse staafje geperst, gevolgd door een Py-GC analyse. De verkregen piekoppervlakken werden genormaliseerd en onderworpen aan multivariate data analyse. Het gebruik van principale componenten analyse (PCA) werd getest op 5 monsters die enigszins verschilden in samenstelling en leeftijd. De resultaten waren veelbelovend en toonden aan dat PCA een belangrijk hulpmiddel is om onderscheid te maken tussen PBX-monsters. De druk waarmee het monster op het pyrolysestaafje geperst werd bleek een belangrijke parameter te zijn. Deze parameter werd geoptimaliseerd samen met de pyrolyse-temperatuur en de hoeveelheid monster. Het optimalisatie-experiment werd uitgevoerd met 2 PBX monsters die slechts verschilden in crosslink dichtheid. Het bleek dat het moeilijk was om optima in de parameters te vinden die resulteerden in een maximaal onderscheid tussen de 2 monsters. De volgende instellingen van de parameters werden geselecteerd: 5,2 ton, 75 µg en 610 °C.

CONTENTS

1 INTRODUCTION

Since 1989 the TNO Prins Maurits Laboratory (TNO-PML) participates for the Netherlands in IEPG TA 25. This project deals with the applicability of current production techniques used in the polymer industry such as injection molding and extruding in the processing of plastic bonded explosives (PBX's). The PBX's studied in TA 25 are based on the commercially available explosives such as cyclotrimethylenetrinitramine (RDX) and cyclotetramethylene-tetranitramine (HMX) and well-known binder systems as hydroxy terminated polybutadiene (HTPB) and isophorone diisocyanate (IPDI). Within TA 25.1 TNO-PML was tasked with the characterization of PBX samples, both with chemical analysis and with shock sensitivity measurements.

In 1987 an investigation was started at TNO-PML to determine whether PBX's could be characterized with Curie point pyrolysis gas chromatography (Py-GC) [1, 2]. The possibilities of Py-GC as a chemical analysis technique in order to detect small differences in PBX's due to variations in composition, age and method of production were investigated. It was shown that a differentiation could be made between aged and unaged PBX samples and that the method was reproducible [2]. These results were obtained with simple statistical t-tests on 4 selected GC-peaks (univariate data analysis). When the discriminative potential of more peaks is combined (multivariate data analysis) a better differentiation between samples may be expected. In the study presented here, the possibilities of multivariate data analysis on the obtained gas chromatograms of PBX samples will be investigated. A short introduction to the multivariate data analysis used is presented in Chapter 3.

It is well known that the pretreatment of the samples as well as the pyrolysis conditions have a great influence on the results [3]. In the previous study the PBX samples were ground and pressed onto a pyrolysis wire using a certain pressure. However, only one pyrolysis temperature (610 °C) and a certain amount of material (35 - 50 μg) were used. No optimization of these parameters had taken place. Therefore a study was performed in order to find the optimum conditions for separation between 2 PBX's which differed only in the crosslink density. The mass of the sample, the pressure by which the sample was pressed on the wire and the pyrolysis temperature were taken into account. An experimental design was used for the planning of these experiments.

Both the use of multivariate data analysis as well as the determination of the optimal pyrolysis conditions must lead to a standard procedure for the Py-GC analysis of PBX's. The developed procedure has to be used as quality control method for the PBX's manufactured within the TA 25.1 project.

2 EXPERIMENTAL PART

2.1 Apparatus and software

The Py-GC system consisted of a Fischer Curie point pyrolyser (type 0316A, 2 kW) interfaced with a Carlo Erba GC (type HRGC 5300). The pyrolysis conditions were as follows: pyrolysis time 1.5 sec, reactor temperature 125 °C, the pyrolysis temperature was varied. The GC conditions were: detector, FID; column, a Chrompack PLOT fused silica, 25 m x 0.53 mm ID and coated with Al_2O_3/KCl; flow rates in ml/min: helium (carrier gas) 3.5, hydrogen 13.0 and air 360; the oven programming was: 45 °C (2 min), R1=25 °C/min, 110 °C (2 min), R2=15 °C/min, 175 °C (5 min), R3=25 °C/min, 200 °C (24 min), 45 °C (6 min).
Details of the interfacing of the Fischer pyrolyser with the Carlo Erba GC are depicted in Figure 1. The removable glass tube (Figure 1, part 6) had the following functions [4, 5]:

- to centre the pyrolysis wire axially as well as longitudinally;
- to reduce the dead volume;
- to trap involatile residues.

Data acquisition: a Minichrom (DEC PC350/VG) data system was used for all experiments except for the optimization measurements which were performed with a Maxima data system (V3.30, Dynamic Solutions).
Data analysis: Lotus 123 (V2.01). Statistical analysis: ARTHUR (Infometrix, Version of January 1981), SPSS/PC+ (SPSS Inc. V3.0) and SSP (DEC, V01.1).
A VG 70-250S mass spectrometer coupled with an HP 5890A gas chromatograph was used for the identification of the GC-peaks. Surface analysis was performed with a Philips scanning electron microscope 515 (SEM).

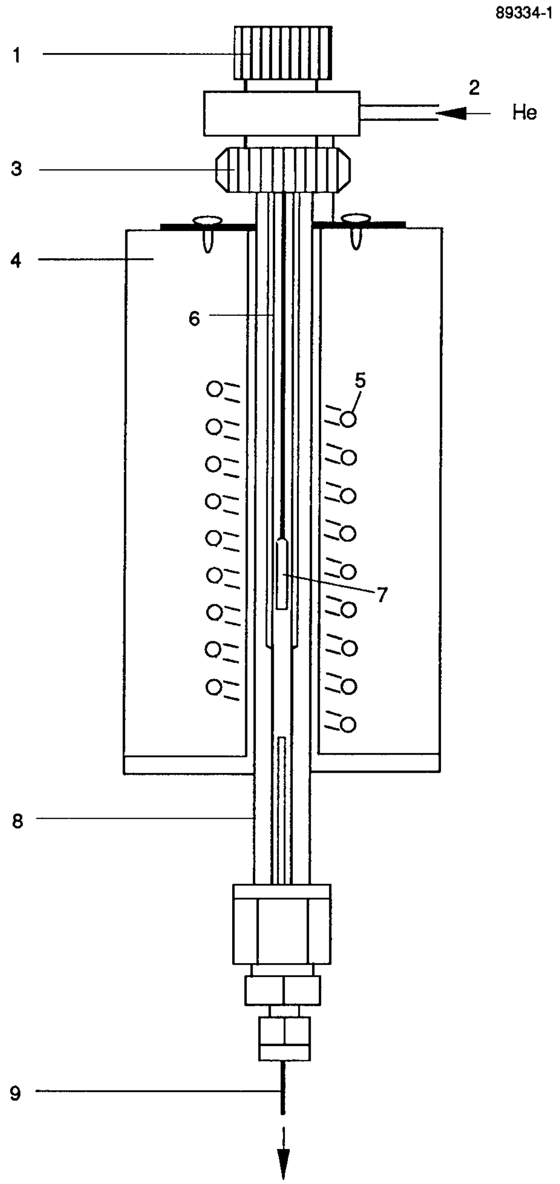

Figure 1 *Interface of the pyrolyser and the GC*

1 screw cap with a septum
2 inlet carrier gas
3 sampler housing
4 pyrolyser reactor
5 induction coil
6 removable glass tube
$l = 105$ mm, ID = 1.55 mm, OD = 2.40 mm
7 pyrolysis wire held by a septum
$l = 64$ mm
8 glass sample holder (OD = 6.40 mm) consisting of 2 parts fused together
($l_1 = 100$ mm, $ID_1 = 2.50$ mm and $l_2 = 30$ mm, $ID_2 = 0.55$ mm)
9 GC column

2.2 Sample preparation

For the sample preparation the same grinding procedure as described earlier was used [2]. The preparation of the pyrolysis wires was, however, somewhat modified as well as the weighing of the PBX samples.

The wires were washed with acetone (Merck p.a.) and n-hexane (Merck p.a.), respectively, and dried overnight in an oven at 250 °C.

Over a length of 14 mm the wire was flattened with a press exerting a pressure of 8.0 tonnes for 30 sec. The wires were pressed between 2 specially prepared, hardened stainless steel discs. On one disc a circle with a radius of the disc minus 14 mm was engraved to ensure the length of the flattened part. In this way a reproducible temperature rise time (TRT) of the wire was obtained. The estimated TRT was around 10 msec [6]. To press a certain amount of a PBX sample on the wire about twice the amount was transferred to one disc. By means of the tip of a spatula the sample was positioned in a very narrow line. This line had a length of 10 mm (2 mm away from both edges of the flattened part of the wire). The flattened part of the preweighed pyrolysis wire was carefully positioned over the sample and fixed in place by laying the second disc on it. In order to avoid contamination of the wire, the unflattened part of the wire was always manipulated with a pair of tweezers. The discs, sample and wire were pressed for 30 sec with a pressure required for the particular experiment. The wire together with the pressed sample was weighed again. In case the amount of sample was too small or the sample was not distributed equally over the flattened end of the wire, the wire was discarded. A small amount of material was scratched off the wire with a spatula if the wire contained too much sample. It was checked that this last procedure had no effect on the pattern of the peaks. After scratching the wire, it was wiped with a lint free tissue to remove small particles which could not be removed by ticking on the pair of tweezers holding the wire. This procedure resulted in a very thin film of compressed PBX particles. The thickness of this film was about 10 μm as measured with a SEM (Figure 2).

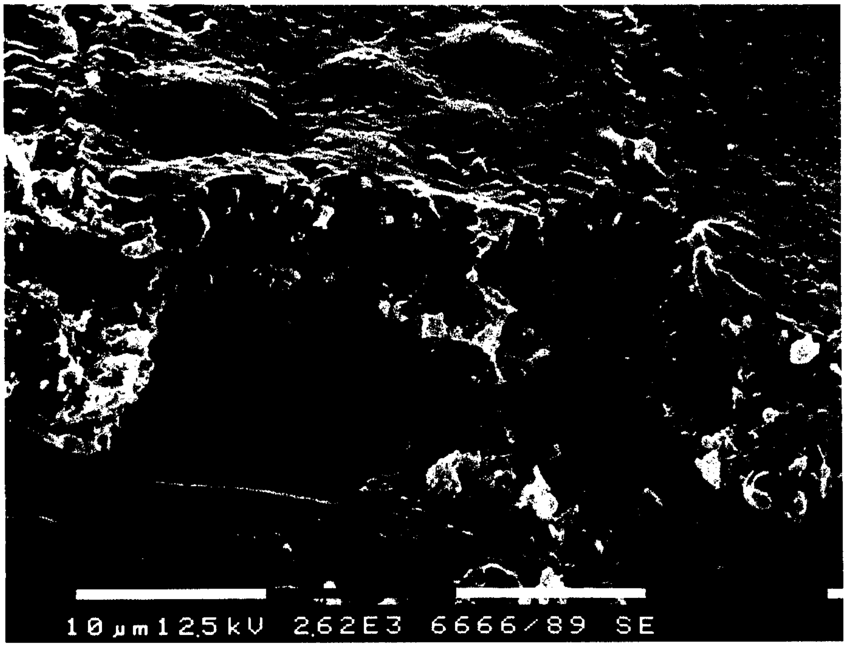

Figure 2 SEM picture of a PBX sample pressed on a pyrolysis wire

In order to obtain a good reproducibility in Curie point pyrolysis, it was essential that the sample was placed correctly in the pyrolysis reactor [5]. The length of a pyrolysis wire was adjusted in such a way that the centre of the flattened part of the wire corresponded with the centre of the pyrolyser reactor (see Figure 1).

2.3 Pyrolysis gas chromatography

Before positioning the pyrolysis wire, a new removable glass tube was placed in the pyrolyser reactor which was allowed to reach the ambient temperature of 125 °C during 3 min. Next the wire, which was held by the septum, was placed in this glass tube. To expel the enclosed air 1.5 min was waited before the sample was pyrolysed. All the analyses were carried out without splitting of the carrier flow. After the GC analysis using the conditions described in paragraph 2.1, the peak areas of the resulting chromatogram were calculated.

2.4 Data treatment

To exclude effects due to small variations in sample size the peak areas were normalized. Each peak area (variable) was divided by the total peak area of the peaks selected for the statistical analysis. Since most types of multivariate data analysis are sensitive to the size of the variables (larger ones are given more weight), all variables were first autoscaled before the statistical analysis. For each variable the average and the standard deviation were calculated over all chromatograms (cases). From each case the average was subtracted and divided by the standard deviation. This was performed for all variables. As a result all variables had a mean of zero and unit variance.

3 MULTIVARIATE DATA ANALYSIS

3.1 Principal component analysis

The fundamentals of Principal Component Analysis (PCA) will be explained from a geometric point of view (see Figure 3) for the sake of clarity. For mathematical details reference is made to text books [7, 8].

Suppose a chromatogram consists of n peaks. Each peak (variable) of the chromatogram (object or case) can be considered as an axis in an n-dimensional space. Consequently each chromatogram can be represented as one point in this space. The total variance in the data is represented by all n axes and is set at 100%. The basic idea of PCA is to reduce the dimensionality of this space to a smaller subspace retaining as much of the variance of the data as possible. This is accomplished by transforming the original variables into a set of uncorrelated (i.e. orthogonal) variables known as principal components (PC's). Figure 3 represents a simple case of PCA in which the origins of the axes of the PC's and of the original variables coincide. In real situations this is very unlikely. The resulting PC's are linear combinations of the original variables and are arranged in order of decreasing variance. The first PC explains as much as possible of the total variance, the second PC accounts for the maximal amount of the remaining variance and so on. If the original variables are highly correlated, the first few PC's are sufficient to reproduce the systematic variance in the data. Random variation is largely represented by the last PC's and is eliminated in this way.

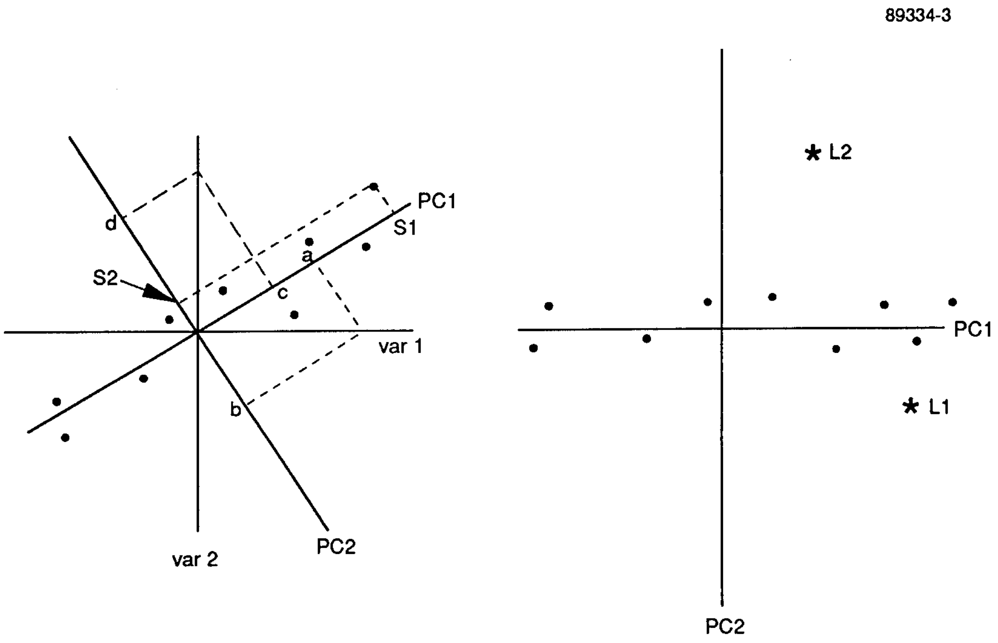

Figure 3 *Example of a PCA score and loading plot*

S_1 = *score on PC1* L_1 = *endpoint of vector* $\begin{pmatrix} a \\ b \end{pmatrix}$

S_2 = *score on PC2* L_2 = *endpoint of vector* $\begin{pmatrix} c \\ d \end{pmatrix}$

The projections of the objects on the PC's are known as scores, the projections of the original variables on the PC's as loadings. The relationship between the objects can be revealed in a score plot in which the scores are plotted in a plane spanned by 2 PC's. The contribution of the variables to the PC's are represented by the loadings, in Figure 3 shown as the direct projections on the PC's. Furthermore, correlated variables have similar loadings on the PC's and appear as a cluster in a loading plot.

3.2 Discriminant analysis

Discriminant analysis (DA) [7, 8] involves deriving linear combinations of the variables that will discriminate between a priori defined groups in such a way that the misclassification error rates are minimized. Each group consists of x objects (x fold measurements). Minimizing the misclassification rates is accomplished by maximizing the between group variance relative to the within group variance. The within group variance for each group is defined as the variance in the objects belonging to the same group. Summing the within group variances yields the total within variance. The between variance is calculated from the average group means of all groups. In case of 2 groups, only one discriminant function (DF) can be calculated. In general if the number of variables (n) exceeds the number of groups (g) then the maximum number of DF is g - 1 otherwise the maximum number is n. The DF's are ranked in descending order of magnitude of their discriminative power. As in PCA, discriminant scores can be calculated by projecting the objects on the DF's resulting in a much more condensed version of the between group differences.

3.3 Distance and similarity measures [8, 9, 10]

The distance between 2 points is a measure of the similarity (or dissimilarity) between them. A well-known example of a distance is the Euclidian distance (ED). For 2 points in an n-dimensional space, $X^T=(a,b,c..)$ and $Y^T=(p,q,r..)$, the squared Euclidian distance is defined as:

$$SED = (a-p)^2 + (b-q)^2 + (c-r)^2 + ...$$

Or in matrix notation:

$$SED = X^T.Y$$

In general uppercase letters represent a matrix or (column) vector, while lowercase letters represent a scalar. The matrix X^T is the transpose of X. The distance matrix contains the distances of all possible combinations of 2 points in an n-dimensional space. Since the points in space are determined by the pattern of the variables, the distance is therefore a similarity measure of the patterns of the 2 points. The SED is considered as a dissimilarity measurement since larger distances reflect a larger difference between the points.

Besides the SED there are other distance measures. The Cosine, which is defined as:

$$\text{Cosine}(X,Y) = (\Sigma X_i Y_i)/\{(\Sigma X_i^2).(\Sigma Y_i^2)\}^{1/2}$$

is particularly useful in measuring the similarity between patterns of variables. X and Y are pattern vectors and i represents summations over all variables (dimensions). For X=Y the Cosine has its maximum value of 1, whereas the minimum value is -1 in the situation when the variables are autoscaled (see paragraph 2.4).

Another criterion for the distance between 2 groups of samples is the Mahalanobis distance (D_M), which is the distance between the groups corrected for the variance within these groups. Suppose 2 groups g_1 and g_2 consist of i and j measurements, respectively. Each measurement can be represented as one point in the n dimensional space (n variables). In each dimension the average of the measurements can be calculated and presented as a scalar. The average of the gi measurements can be represented as a vector Ag_1, in which the first row is the average of the measurements in the first dimension, the second row the average of the second dimension etc. For the j measurements the calculation is similar. The Euclidian distance, $Ag_1^T.Ag_2$, does not account at all for any variance in the data. It does not matter whether the 2 groups overlap each other (large variance) or are well separated (small variance), as long as the averages of the groups remain the same. The Mahalanobis distance, however, also accounts for the variance in the groups and is calculated in the following manner: $D_M^2 = Ag_1^T.S^{-1}.Ag_2$, where S^{-1} is the inverse of the pooled within group variance of g_1 and g_2. From this equation it can be inferred that a larger variance will result in a smaller Mahalanobis distance. The within group variances of g_1 and g_2 are represented by S_1 and S_2, whereas S is the sum of S_1 and S_2. In the case that n exceeds (i+j-2), the inverse of the matrix S does not exist since the rank of the matrix S is (i+j-2) which is smaller than n (dimension of S is n*n). However, an estimation can be made of the inverse of S which is called the generalized inverse S^-.

3.4 Experimental design [11, 12, 13]

An investigation of the effects of several parameters has traditionally relied on the “one variable at a time” approach. This can, however, produce incorrect results since interactive effects between parameters cannot be revealed. Another reason to use a design is one of efficiency because the traditional approach may require much more experimental work in comparison with a correct designed experiment. The relationship between a response parameter Y and the predictor parameters $X_1..X_n$ can be revealed with a first or higher order design. In a first order design only a relationship of the form $Y = b_1X_1 + .. + b_nX_n$ can be established. A full second order design also determines the coefficients of the quadratic terms $(X_1^2..X_n^2)$ and of the interactive terms (for instance $X_1.X_2$). It is important to note that no physical or chemical meaning should be ascribed to an individual term in the empirical model unless there is a sound theoretical reason to do so.

In planning a design it is important which parameters (factors) should be investigated. Each factor is measured on a few levels which determine the order of a design. The highest order polynomial that can be estimated from a design in which each factor is measured at 2 levels is one. When a second order polynomial is desired each factor has to be measured at least at 3 levels. Because of statistical reasons the levels have to be equidistant (rotatable design): for example the factor temperature is measured for instance at 100, 200 and 300 °C. However, it is unnecessary for a useful design to be exactly rotatable. As a transformation is performed on the actual levels, they are represented by -1, 0 and 1. From each actual level the mean of the factor levels is subtracted and the result is divided by the distance between the levels.

In order to rule out unspecified disturbances (for example instrumental drift), the experiments have to be performed randomly i.e. the order, in which the combinations of the levels are measured, is randomised. At the level 0,0,0 (the centre point), more than one measurement is performed (replicates) which are used to test the lack of fit of the model.

4 RESULTS AND DISCUSSION

4.1 General

The primary aim of this study was the optimalization of the parameters controlling the pyrolysis conditions of the investigated PBX samples. However, not all the parameters were systematically investigated. The pyrolysis time and pyrolyser reactor temperature (ambient temperature) were preselected. In the range of 100 °C to 200 °C the ambient temperature had no influence on the pattern of the peaks, since only low molecular pyrolysis products were analysed [3]. Because RDX starts to decompose in the temperature region of 190 to 210 °C [14], the reactor temperature was chosen well below this point and was kept at 125 °C. Since the pyrolyser and the GC oven were interfaced close together, the reactor temperature was influenced by the heat of the oven. Therefore, the reactor temperature could not be set at a lower temperature. A pyrolysis time of 1.5 sec was chosen. A higher setting of this parameter had little or no effect on the results.

The temperature at which the pyrolysis is just complete can be considered as the most suited pyrolysis temperature. This temperature is defined as $T_S + \theta$, where T_S is the characteristic temperature defined as that temperature at which a fraction 1/e (≈37%) of the sample remains unpyrolysed [5]. To determine T_S for PBX samples, 4 pieces were taken from a HMX based PBX sample (code H23) and pyrolysed at 4 different temperatures. The temperatures selected, based on the available pyrolysis wires, were 358, 450, 510 and 610 °C. Amounts of 100 µg of PBX were pressed at the wires with 5.2 tonnes. The amounts of the residues were estimated with a SEM. As the weights of the residues of the samples were so small they could not be determined exactly. The residues at the pyrolysis temperatures of 358 °C and 450 °C are shown in Figure 4. At these temperatures the pyrolysis was clearly incomplete. The pyrolysis was nearly complete at 510 °C and complete at 610 °C. For the determination of T_S only a rough estimate of around 500 °C could be made. With a temperature rise time (TRT) of about 10 ms a normal value of θ is 30 to 40 °C, which leads to a pyrolysis temperature of 540 °C.

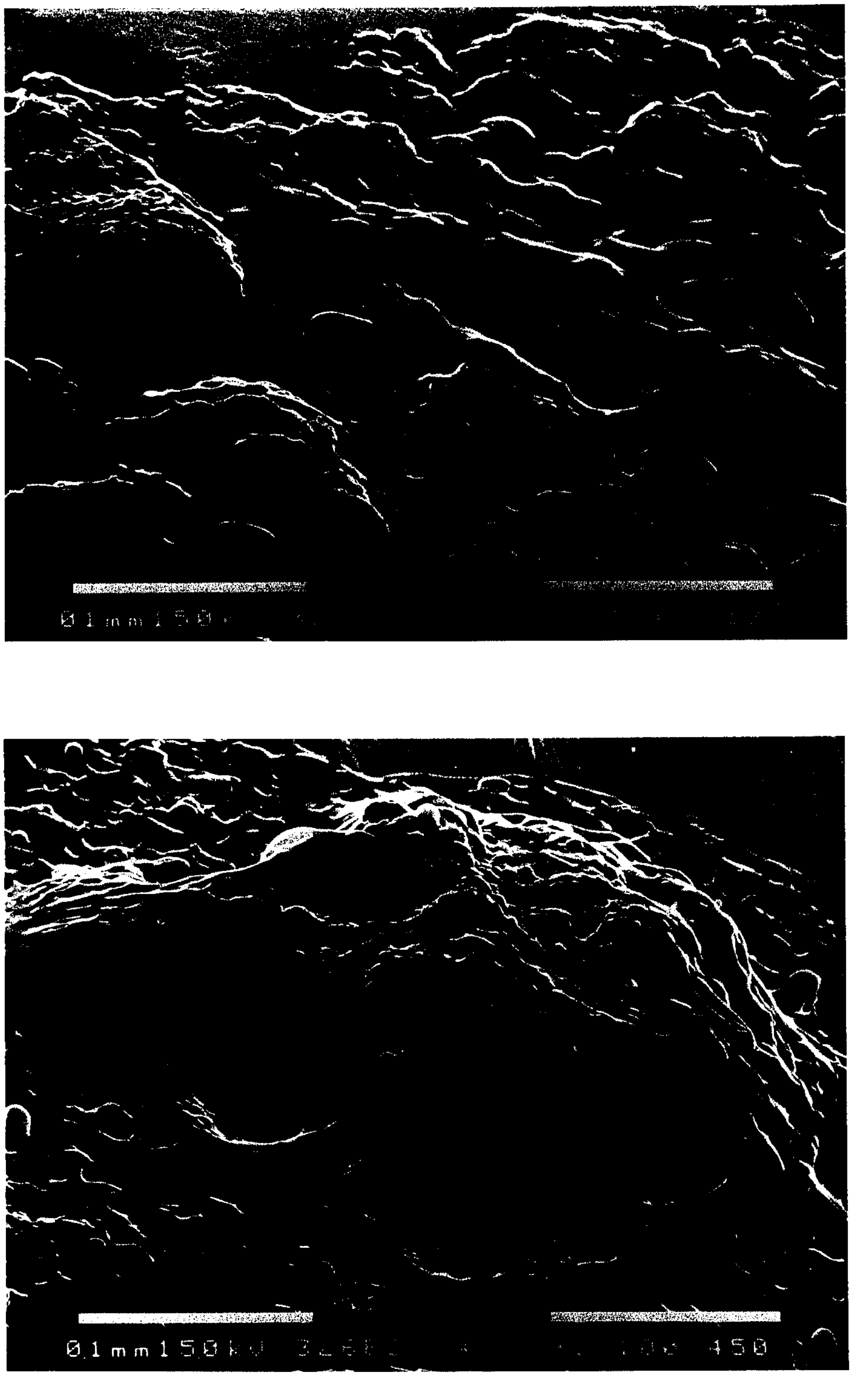

Figure 4 *SEM pictures of the residues of a PBX sample pyrolysed at 358 °C and 450 °C*

The thickness of the sample layer on the wire is normally about 10 μm before pyrolysis. As can be deduced from Figure 4 the thickness of the residual layers at the pyrolysis temperatures of 358 and 410 °C is far greater than this value. The weight of the residue was less than 15 μg. Since the mass of the PBX sample (containing 85% HMX) was about 100 μg the mass of the polymeric binder corresponded with about 15 μg. One may conclude that the binder and the explosive pyrolyse more or less independent from each other. The explosive decomposes at far lower temperatures compared to the binder. This is not surprising since the heat flux from the gas phase reaction zone to the solid phase is small [15]. The temperature at the top layer of the solid phase is approximately the decomposition temperature of the explosive, which is 280 °C for HMX. Furthermore, during the decomposition of the explosive material gases are released under relative high pressure, which explains the foamy structure of the residue at low pyrolysis temperatures [16]. In the case of pyrolysis, the temperature of the PBX sample is determined by the temperature of the pyrolysis wire. For temperatures as low as 358 °C, HMX will decompose more or less independent from the binder. Only at high enough pyrolysis temperatures the binder also decomposes.

During preliminary experiments it was found that the reproducibility of the measurements improved when masses larger than 50 μg were analysed. Going from 50 μg to 200 μg the coefficient of variation decreased from ca. 10% to ca. 7%. This effect is probably caused by the inhomogeneity of the sample [17] since the reversed is expected due to the less homogeneous temperature distribution in a larger sample [3,18]. It was found that the total peak area was directly proportional to the amount of sample pyrolysed, at least up to 200 μg. Even for these relatively large samples the pyrolysis was complete and no secondary reaction products were observed in the chromatograms. However, as will be explained later in paragraph 4.3.3, the pattern of the peaks was slightly dependent on the mass. Since masses could be weighed only with an accuracy of +/-15 μg, this may also account for part of the improved reproducibility when higher masses were pyrolysed.

When samples were placed in the pyrolyser it was inevitable that air was introduced into the Py-GC system. As a result some moisture was flowing through the GC column (packed with Al_2O_3/KCl), leading to an increase in the retention times of the peaks. When the column was conditioned at 200 °C for 1 hour the effect disappeared and the retention times returned to their original values. The increase in the retention times was not the same for all peaks what hindered the identification of peaks with retention times above 11 min. Consequently, in comparing different samples only the first part of the chromatograms were normally used for the data analysis. In case when more peaks have to be selected, identification by means of gas chromatography-mass spectrometry (GC-MS) will be necessary. This was done once to characterize the major peaks. A typical example of a chromatogram is presented in Figure 5; the identified compounds are given in Table 1. All the identified compounds are hydrocarbons, which for the greater part originate from the polymeric binder. This indicates that with the present Py-GC method only variations in the polymer and its additives can be traced.

Table 1 *GC peaks used for the data analysis*

No.	Retention time (min)	Compound
1	1.5	methane[1]
2	1.8	ethane
3	1.9	unknown
4	2.0	ethene
5	2.8	propane
6	3.9	propene
7	4.4	acetylene
8	4.7	unresolved peak[2]
9	5.0	n-butane
10	6.1	trans-2-butene
11	6.2	1-butene
12	6.5	2-methylpropene
13	6.8	cis-2-butene
14	6.9	unknown
15	7.5	unknown
16	7.7	cyclopentane
17	8.0	1,3-butadiene
18	8.7	cyclopentene
19	8.9	C_5H_{10}
20	9.0	C_5H_{10}
21	9.3	C_5H_{10}
22	9.5	C_5H_{10}
23	9.9	C_5H_8
24	10.0	methylcyclopentane
25	10.4	unresolved peak[2]
26	10.8	C_5H_6
27	10.9	n-hexane
28	21	unknown
29	23	probably ethylbenzene
30	24	probably (m- or p-) xylene
31	29	unknown

[1] Could not be identified by GC-MS because it was overwhelmed by the peaks of NO and N_2O, but the retention time corresponded with that of methane.

[2] Due to insufficient GC resolution, the area of more than one peak was taken.

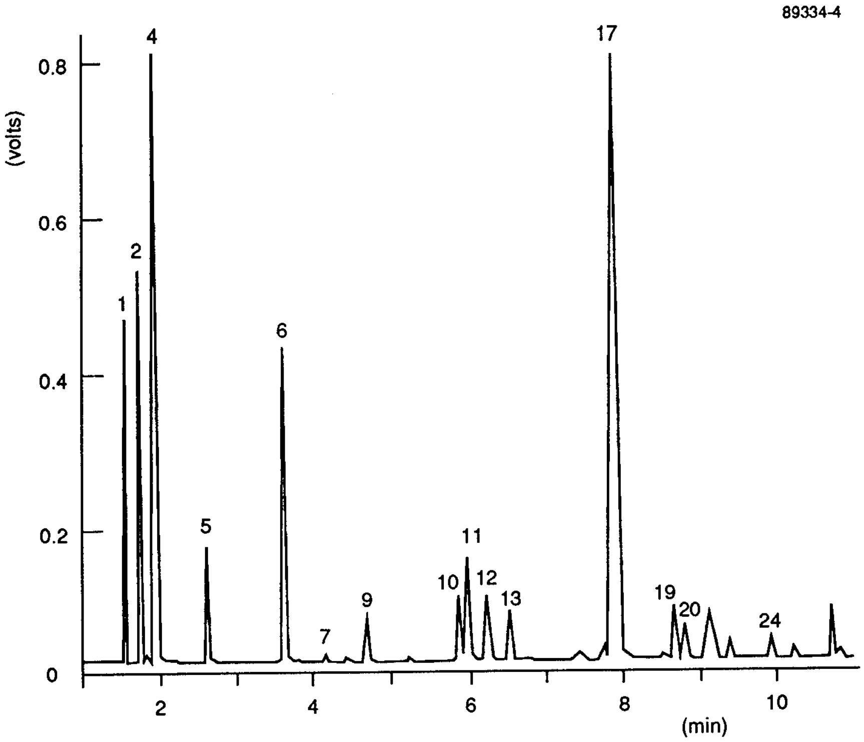

Figure 5 *An example of a chromatogram obtained after the Py-GC analysis of a PBX sample*

4.2 PCA applied to 5 samples

In order to demonstrate the possibilities of PCA, it was applied to the chromatograms obtained after the pyrolysis of 5 PBX samples. For this preliminary experiment only the first 15 largest peaks of the chromatograms were taken into account. These peaks correspond with the nos. 1 up to 20, excluding nos. 3, 8, 13, 14 and 15 from Table 1. Each PBX sample was measured in sixfold (30 measurements). Details of the sample compositions are given in Table 2.

Table 2 Composition and characteristics of 5 PBX samples[1]

Code	H23	H24	R50	R63	R74
HMX	85%	85%	-	-	-
RDX	-	-	85%	85%	85%
Flexzone[2]	-	-	0.10%	-	0.01%
DTBHQ[2]	0.10%	0.10%	-	0.10%	-
NCO/OH[3]	0.80	1.10	0.99	0.96	1.00
age(yrs)	3.4	3.5	4	3	0.6

1 The PBX were prepared at TNO-PML according to procedures described elsewhere [19]. The samples were cured at 60 °C during one week.

2 The antioxidants Flexzone and DTBHQ are N-phenyl-N'-cyclohexyl-p-phenylenediamine and di-t-butylhydroquinone, respectively.

3 NCO/OH is the equivalence ratio of the isocyanate groups from IPDI and the OH groups from HTPB, which is a measure of the number of crosslinks per volume (crosslink density) of the polymer.

The samples H23 and H24 differed only in the crosslink density of the polymeric binder, while the other samples were more different. A pyrolysis temperature of 610 °C and a mass of 200 μg was applied. In contrast with the previous study [2], where a pressure of 6.1 tonnes was used, the pressure was reduced to 2.3 tonnes, because with 6.1 tonnes the samples did not stick well to the wire (see footnote).

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1 After calibration of the press it was found that the readings deviated to a relative large extent from the real values. This explains the somewhat unusual pressures used in this investigation.

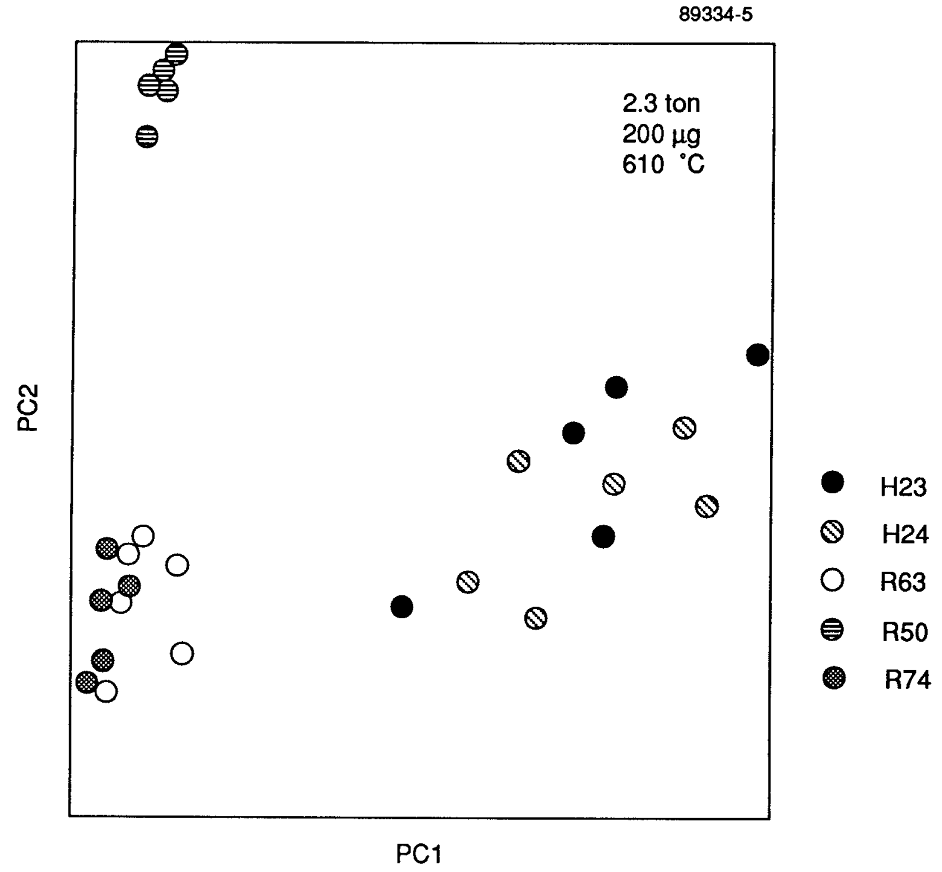

Figure 6 *Score plot of 5 samples after applying a pressure of 2.3 tonnes (95% of the total variance explained)*

From the obtained score plot of PC1 versus PC2 (Figure 6) it is obvious that the samples were incompletely separated, especially H23 and H24. This was unexpected in view of the previous results [2] and could perhaps be attributed to the larger mass or to the reduced pressure applied. To check the effect of the pressure, the samples were measured again using 5.2 tonnes to press a 200 µg sample on the wire. The results of the PCA are presented in Figure 7.

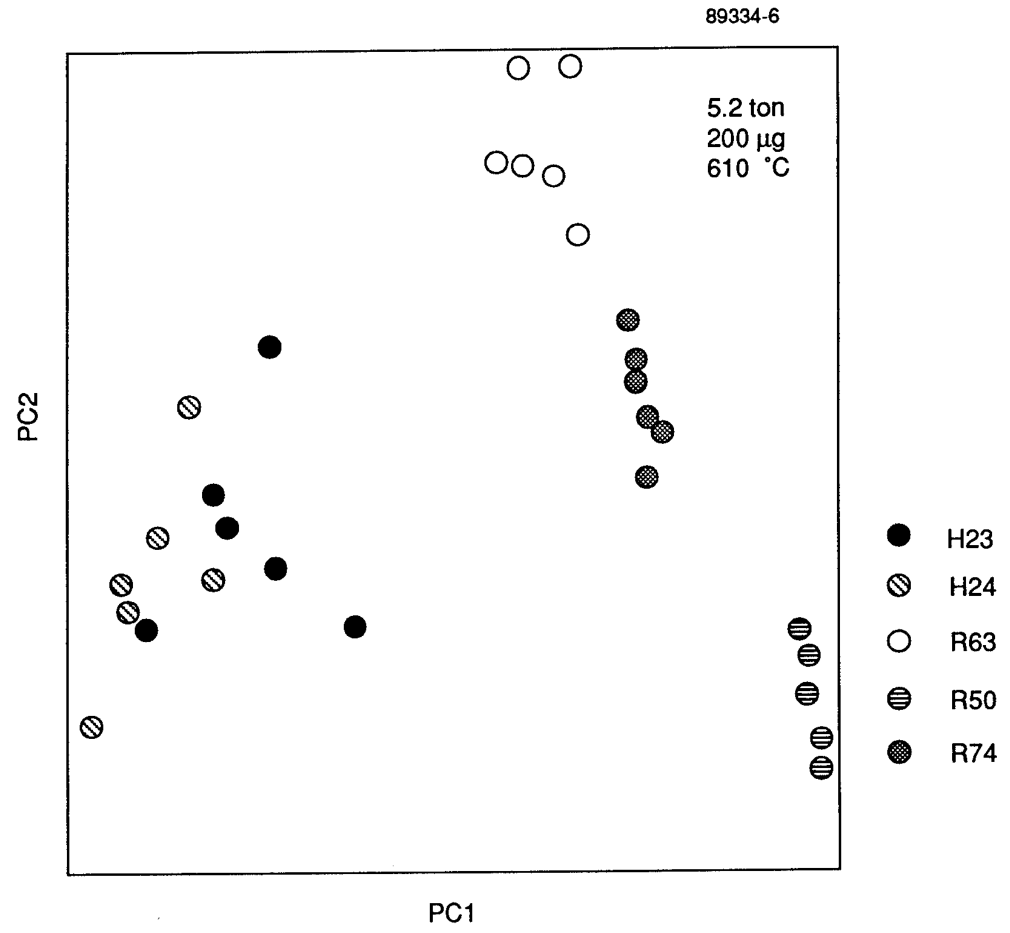

Figure 7 *Score plot of 5 samples applying a pressure of 5.2 tonnes (94% of the total variance explained)*

Compared to Figure 6 there is a better discrimination between the samples applying a pressure of 5.2 tonnes, and it may be concluded that the pressure is an important parameter in order to differentiate PBX samples. The samples H23 and H24 were also pyrolysed after pressing them on a wire with 9.9 tonnes. An increase in the pressure of 2.3 to 5.2 tonnes increased the differentiation between the 2 samples. However, exerting a pressure of 9.9 tonnes on the sample, did not lead to an even greater differentiation. Therefore, one may conclude that an optimum in the parameter pressure exists. This effect cannot be properly explained. Applying larger pressures gives thinner sample films and improves the contact between the sample and the wire, which results in an increase of the heat transfer from the wire to the sample leading to more intense GC-peaks. However, this does not explain why the differentiation between the 2 samples was dependent on the pressure as found here.

4.3 Optimization of the pyrolysis conditions

4.3.1 Parameters, samples and peak selection

Based on the results of the experiments described in paragraph 4.2 it was decided to carry out an optimization experiment. In addition to the pressure (P), the pyrolysis temperature (T) and the amount (mass) of the sample (M) were studied. These 3 parameters were taken into account to find out what their influence was on the differentiation between 2 PBX samples. Moreover, from the dependency of the mass on the results the accuracy by which the samples have to be weighed could possibly be deduced.

The samples H23 and H24, which differed only in crosslink density, were difficult to separate by means of PCA (see paragraph 4.2). Therefore these 2 samples were selected for the optimization experiment, which must result in the determination of those levels of the parameters leading to the largest separation. As the samples H23 and H24 were very similar it will be assumed that the determined optimum conditions holds for every other sample. However, the effect of the parameters does not necessarily have to be the same for other samples. The 2 selected samples were both ground about 10 months before the start of the analysis and were measured over a period of 7 weeks. During these 7 weeks the effect of ageing will be relatively small. Since ground samples age more rapidly compared to original samples, this optimization study was performed on relatively 'old' samples. It was assumed that the 2 samples aged equally. In this way sample variations were excluded as well.

Not all the 31 GC peaks given in Table 1 were used. Due to mathematical reasons the number of peaks had to be reduced. Based on a univariate t-test 9 peaks were selected which contributed most to the discrimination between the 2 samples. These peaks corresponded with the peak nos. 2, 14, 19, 24, 27, 28, 29, 30, 31 of Table 1. Most of the selected 9 GC peaks had retention times above 11 min indicating that the larger degradation products contain more specific information on the samples. Since the chromatograms of both samples showed a strong resemblance the advisable identification of the GC peaks above 11 min by GC-MS was not needed.

The following boundaries of the parameters were chosen:

- Temperature (T). As explained in paragraph 4.1 a minimum temperature is necessary for a complete pyrolysis. If on the other hand the temperature is too high samples decompose more randomly and the polymers pyrolyse similarly [5, 20]. The levels of the parameter temperature were set at 510 °C, 650 °C and 770 °C.
- Mass (M). Due to weighing problems an amount of 50 µg was the lowest mass taken. Since with 200 µg samples sticking problems occurred during pressing, 150 µg was the highest mass tested.
- Pressure (P). To attach an amount of the sample on the wire a certain pressure is needed. Applying a lower pressure than 2.3 tonnes seemed illogical in view of the previous results (see paragraph 4.2). The lowest pressure chosen was 4.2 tonnes. The highest pressure was determined by practical considerations. By using a pressure above 9.9 tonnes the wires became very flattened and consequently did not fit in the glass tube of the pyrolyser reactor. Therefore, the highest pressure applied was 8.0 tonnes.

4.3.2 Experimental design

Since an optimum in the parameter pressure was expected, a second order experimental design was chosen to study the influence of the 3 selected parameters. A Box-Behnken design with a redundancy factor of 1.6 when 4 centre points are taken, was chosen [12, 13, 21]. In this design the 3 parameters are measured at 3 levels. In Table 3 the details of the design are presented.

Table 3 *A Box-Behnken design at 3 factor levels and 3 variables (pressure, mass and temperature)*

Factor level[1]				
P[2]	M[3]	T[4]	Exp. No.	Calculated Mahalanobis distance
1	1	0	15	11.1
1	-1	0	11	3.5
-1	1	0	6	12.1
-1	-1	0	2	4.9
1	0	1	1	3.4
1	0	-1	4	6.6
-1	0	1	9	5.4
-1	0	-1	14	3.8
0	1	1	13	6.8
0	1	-1	16	6.6
0	-1	1	7	21.9
0	-1	-1	5	6.9
0	0	0	3	7.2
0	0	0	8	6.0
0	0	0	10	7.4
0	0	0	12	3.5
-1	-1	0	17	6.7
0	0	0	18	4.6
1	1	-1	19	8.5

[1] Note that the midpoint of 510 °C and 770 °C is 640 °C instead of 650 °C which makes this design not exactly rotatable

[2] -1 (4.2 tonnes), 0 (6.1 tonnes), +1 (8.0 tonnes)

[3] -1 (50 μg), 0 (100 μg), +1 (150 μg)

[4] -1 (510 °C), 0 (650 °C), +1 (770 °C)

After randomisation, the order in which the experiments were carried out, is given by the fourth column of Table 3. Three measurements (Exp. no. 17, 18 and 19) were additionally performed. At the level (0, 0, 0), 5 measurements were performed which gives 4 degrees of freedom for the lack of fit test. At each level combination both samples H23 and H24 were measured in threefold, leads in total to 114 measurements.

For the determination of the optimum parameter levels separating the samples H23 and H24, the Mahalanobis distance (D_M, see paragraph 3.3) was used as a criterion. This distance measure was selected since a dependence of the variance from the mass was established (see paragraph 4.1). Whether the variance was dependent of the parameters P and T was unknown. For each level combination (see Table 3), this distance was calculated between the 2 groups. Since in this investigation the number of variables is 9 and the number of measurements at each level combination is 6 (both samples measured in threefold), D_M was calculated for each level combination using the generalized inverse of the pooled within group variance matrix S [10].

4.3.3 Effect of the parameters on the pattern of the peaks

The results of the optimization experiment were first subjected to a PCA to reveal the effects of the different parameters. The obtained score plot is presented in Figure 8 and shows the average of each sample at each level combination.

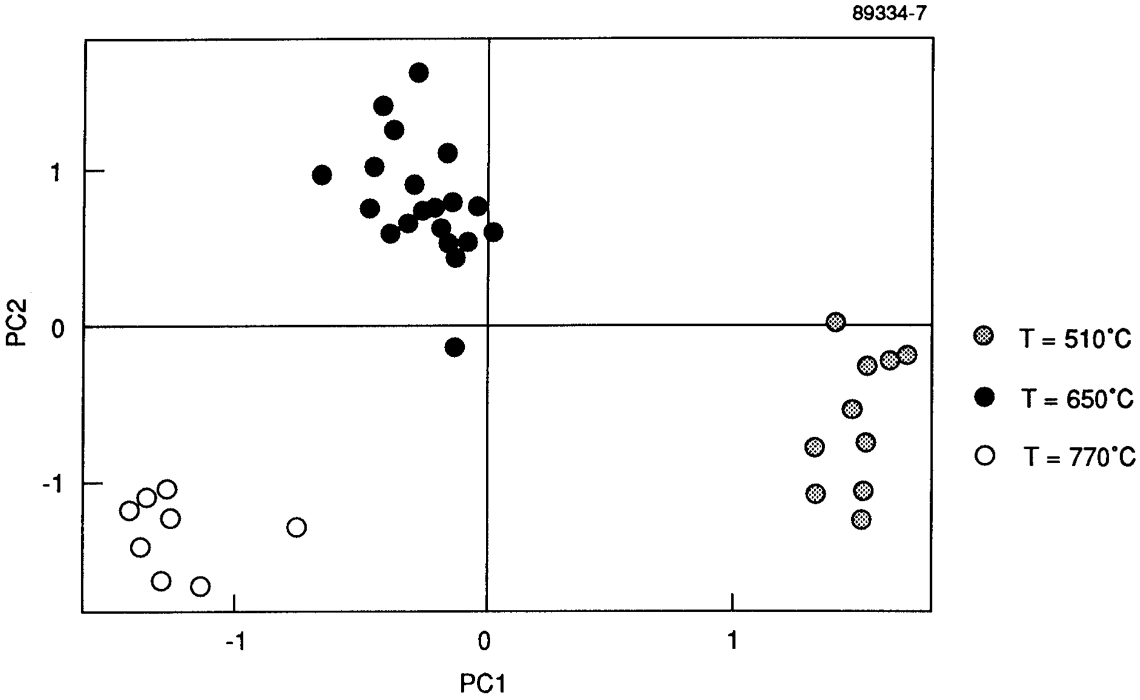

Figure 8 *Score plot of the whole data set of the optimization experiment*

It is evident that the major part of the total variance is caused by the temperature. The measurements at the 3 different temperatures appear as 3 distinct clusters. To understand something about the influences of the parameters mass and pressure, PCA was applied to the samples within each of the 3 clusters. In this way the overwhelming effect of the temperature was eliminated. Since most measurements were carried out at 650 °C, the results are reported for this temperature only (Figure 9). The same conclusions can be drawn for the other temperatures.

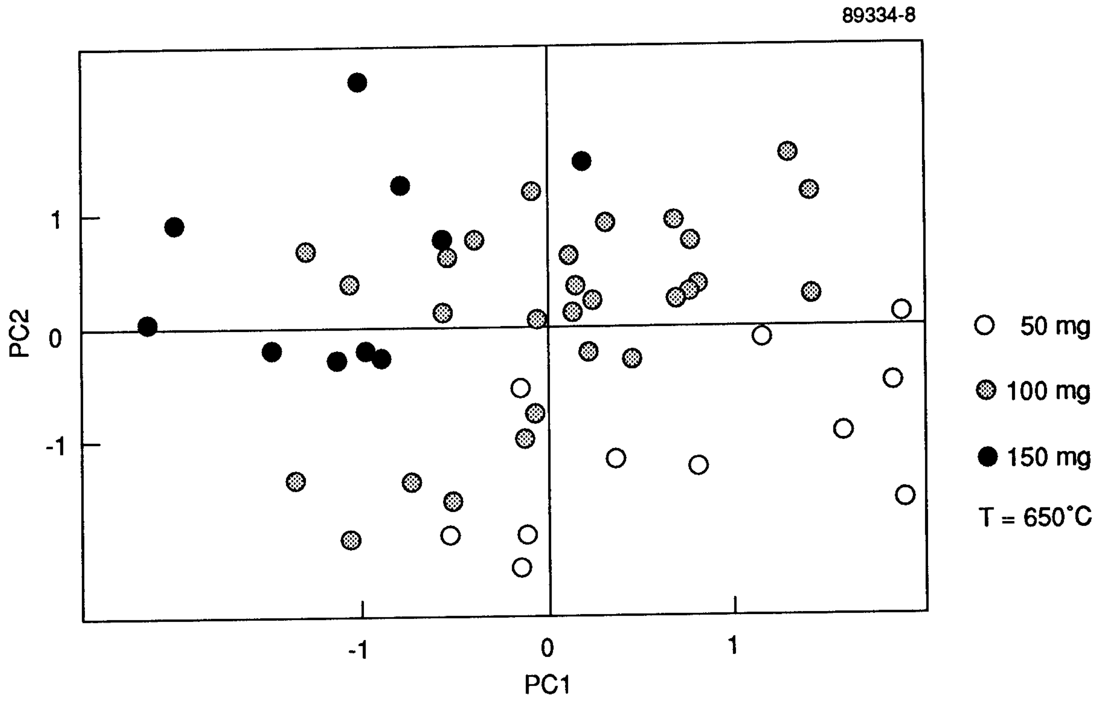

Figure 9 *Score plot of the samples H23 an H24 measured at 650 °C*

It can be inferred from Figure 9, that the mass had also influence on the pattern of the peaks. This means that PBX samples should be weighed within a specified range (+/- 15 µg). Unfortunately, no conclusions can be drawn for the parameter pressure from Figure 9 or from the score plot spanned by PC3 and PC4. This means that the pressure had little or no effect on the pattern of the 9 selected peaks. The effect of the pressure on the differentiation between PBX samples cannot directly be extracted from Figure 9 and will be revealed by the use of DA and multiple regression analysis (see paragraph 4.3.4).

4.3.4 Determination of the optimum parameters levels

The Mahalanobis distances, as tabulated in Table 3, were fitted in a second order polynomial in the parameters P, M and T of the form:

$$D_M = b_0 + b_pP + b_mM + b_tT + b_{pp}P^2 + b_{mm}M^2 + b_{tt}T^2 + b_{pm}PM + b_{pt}PT + b_{mt}MT \qquad (1)$$

The first multiple regression analysis, in which equation (1) was tested, showed that the coefficients b_m and b_{pm} were insignificant (p levels 0.88 and 0.84, respectively). Consequently they were not taken into account during the further analysis. The measurements from experiment number 7 ($D_M = 21.9$) were regarded as outliers. The regression equation was recalculated without the parameters M and PM and discarding measurement no. 7 of which the results are presented in Table 4. The constant b0 was also insignificant but is irrelevant in determining the optimum conditions since it is removed by differentiation (see eq. (2) to (4)).

Table 4 Coefficients of the multiple regression equation

	Standard error	Significance (p level)
b_0 = -6.3	23	0.79
b_p = -8.2	3	0.02
b_t = 0.11	0.06	0.09
b_{pp} = 0.29	0.2	0.19
b_{mm} = 0.00054	0.3	0.06
b_{tt} = -0.00013	0.00005	0.02
b_{pt} = 0.0094	0.0004	0.04
b_{mt} = -0.00018	0.00008	0.05

			Significance (p level)
Statistics [12]:	$F_{goodness}$ of fit = 4.7	→	0.014
	Flack of fit = 1.02	→	>0.25
	Correlation coefficient	(R) = 0.88	

From the statistical analysis it appears that this model proved to be well as the goodness of fit is significant while the lack of fit is highly insignificant. However, the confidence intervals for the coefficients were broad. As a consequence, only a tentative conclusion can be drawn for the optimum levels of the parameters.

To determine the optima, equation (1) is partial differentiated to P, M and T.

$$\delta D_M/\delta P = -8.2 + 0.00094T + 0.59P \qquad (2)$$

$$\delta D_M/\delta M = 0.00011M - 0.00018T \qquad (3)$$

$$\delta D_M/\delta T = 0.11 - 0.00025T + 0.0094P - 0.00018M \qquad (4)$$

Unfortunately, no maximum could be found for the parameter P but instead a minimum was obtained. This minimum is dependent on T and a few numbers are given:

P_{min} = 5.9 tonnes at T = 500 °C
P_{min} = 4.3 tonnes at T = 600 °C
P_{min} = 2.7 tonnes at T = 700 °C.

Within the boundaries of this design the best differentiation between the 2 samples is achieved by applying high pressures (P = 8.0 tonnes). Higher masses also lead to a better differentiation but the effect of the mass is small. Therefore, this parameter will be set at 75 μg for the practical reason of having lesser sticking problems by pressing PBX's on the wire. For the parameter T there appears to be a maximum which can be estimated at 680 °C (P = 8.0 tonnes and M = 75 μg). However, the confidence intervals for the optima were broad (see Table 4). Furthermore, as described in paragraph 4.1, the most suited pyrolysis temperature was estimated at about 540 °C. In view of these results the previously chosen pyrolysis temperature of 610 °C will be a good compromise [2]. Therefore, the pressure is the only parameter that will be validated.

4.3.5 Validation of the optimum conditions

The same 5 samples, as described in paragraph 4.2, were pyrolysed again in fourfold under the conditions of 8.0 tonnes, 75 μg and 610 °C. It has to be noticed that for this experiment, in contrast with that described in paragraph 4.2, all the samples were ground one day before the pyrolysis. Therefore the samples were measured again at 2.3 and 5.2 tonnes under this new, so-called standard procedure. The score plots of the PCA are shown in Figure 10.

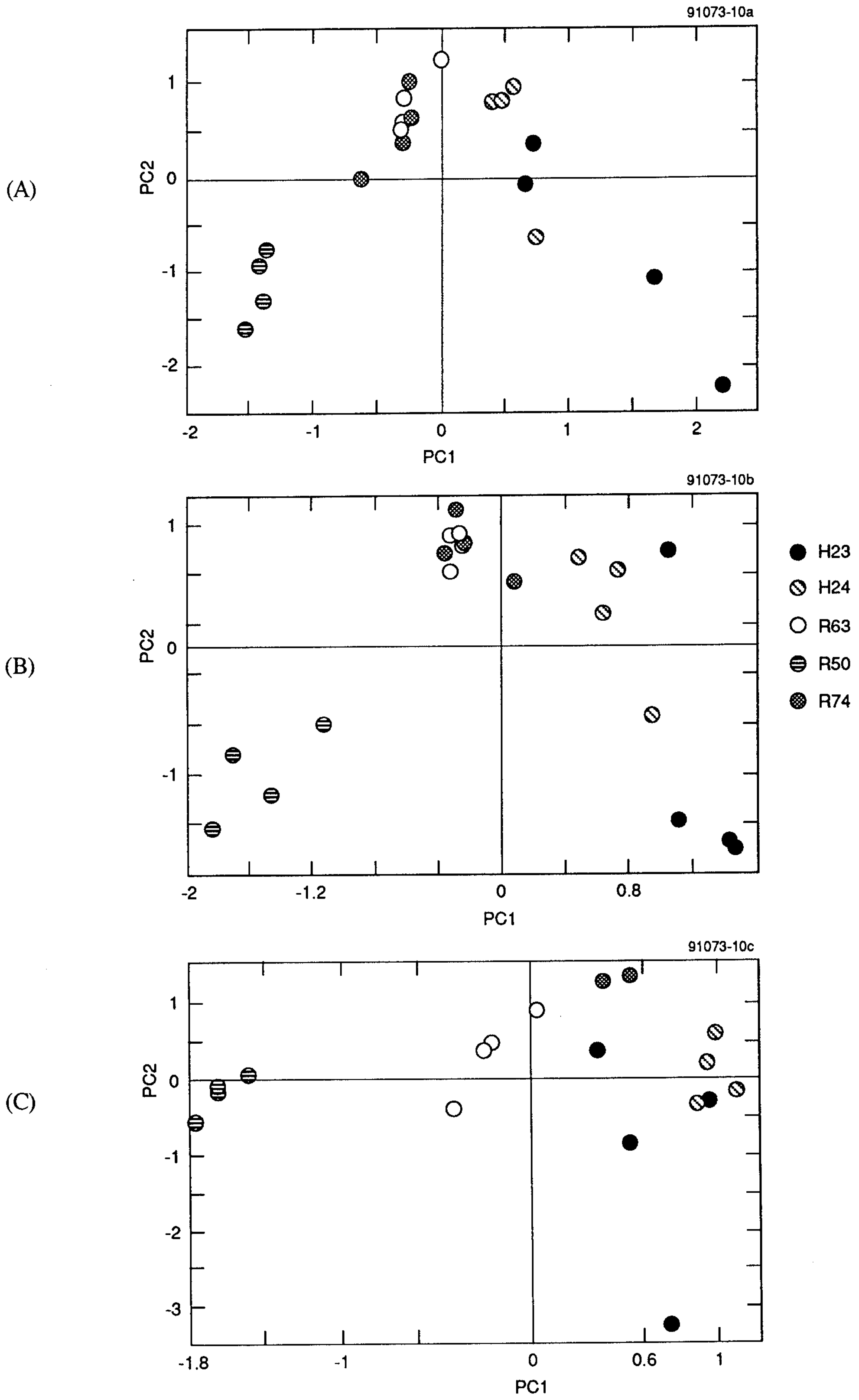

Figure 10 *Score plots of the results of a PCA on the data sets obtained under the conditions of 2.3 (A), 5.2 (B) and 8.0 (C) tonnes and freshly ground samples*

From Figure 10 it can be seen that the samples H23 and H24 are separated equally well under the conditions of 8.0 tonnes and 5.2 tonnes (see also Table 5). However, the separation was not the same for all sample pairs. When the results are compared with those shown in Figures 6 and 7, it is clear that the effect of the pressure was essentially the same. This indicates that the effect of the pressure was identical for freshly ground samples as for old ground samples. This supports the results of the optimization experiment which was carried out with old samples.

The first 27 peaks, as listed in Table 1, were selected for the PCA. The last 4 peaks were not used because of identification problems. The conclusions of the optimization experiment were based on 9 preselected peaks, whereas the results in Figure 10 were based on 27 peaks. Thus the information present in these 9 preselected peaks was also present in the remaining peaks. Therefore, the same conclusions will be obtain when other peaks are taken into account.

For the 2 samples chosen (H23 and H24) in the optimization experiment, the optimum pressure was found to be 8.0 tonnes. In Table 5 it is demonstrated that, within accuracy limits, there was no major difference between the Mahalanobis distances calculated for these 2 samples H23 and H24 at 5.2 and 8.0 tonnes. In order to deduce the best pressure, the Mahalanobis distances were calculated between all possible sample pairs. For the 5 samples at each pressure a PCA was performed and from the scores on the first 3 PC's, covering about 95% of the total variance, the Mahalanobis distance was calculated using the SPSS Discriminant Analysis routine [9]. In Table 5 the results are presented from which it can be concluded that a pressure of 5.2 tonnes seems to be a reasonable choice.

Table 5 *Calculated Mahalanobis distances between all sample pairs*[1]

Between samples	2.3 tonnes	5.2 tonnes	8.0 tonnes
1 and 2	113	521	1603
1 and 3	1	3	160
1 and 4	14	208	108
1 and 5	284	208	65
2 and 3	150	541	1854
2 and 4	158	748	362
2 and 5	485	768	764
3 and 4	11	229	17
3 and 5	40	203	153
4 and 5	2	9	11

[1] 1 = R74   4 = H23
2 = R50   5 = H24
3 = R63

Based on the results of the optimization experiment it seems that the settings of the parameters used in the previous study [2] (6.1 tonnes, 610 °C and 50 µg) can be slightly improved. The parameters will be set at 5.2 tonnes, 75 µg and 610 °C.

5 CONCLUSIONS

A method for the characterization of PBX samples, based on Py-GC analysis followed by PCA on normalized peak areas, was developed. It was demonstrated that with this method a differentiation can be made between PBX samples, which differ only to a minimum extent in composition and properties (for instance crosslink density, age). The differentiation was found to be dependent on the parameters pressure, the amount of sample and the pyrolysis temperature. The optimum conditions for the differentiation between PBX samples were estimated and found to be 5.2 tonnes, 75 μg and 610 °C. Because the mass has influence on the pattern of the GC peaks, PBX samples have to be weighed within a specified range (+/- 15 μg) before the Py-GC analysis.

6 AUTHENTICATION

E.R.J. Wils
(Project Leader)

M. Rietjens
(Author)

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11. AUTHOR(S)

M. Rietjens

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TNO Prins Maurits Laboratory, Lange Kleiweg 137
P.O. Box 45, 2280AA Rijswijk, The Netherlands

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15. ABSTRACT (MAXIMUM 200 WORDS (1044 BYTE))

A further development of the procedure based on pyrolysis-gas chromatography (Py-GC) for the characterization of plastic bonded explosives (PBX's) is described. After grinding, the PBX samples were pressed on a pyrolysis wire followed by Py-GC analysis. The peak areas obtained were normalized and submitted to multivariate data analysis. The use of principal component analysis (PCA) was tested on 5 samples which differed slightly in composition and age. The results were promising and showed that PCA is a powerful tool for the differentiation between PBX samples. The pressure by which the samples were pressed on the pyrolysis wire appeared to be an important parameter. This parameter was optimized together with the pyrolysis temperature and the amount of sample. The optimization experiment was carried out with 2 PBX samples which differed only in crosslink density. It turned out that it was difficult to find optima in the parameters resulting in a maximal difference between the 2 samples. The following settings of the parameters were selected: 5.2 tonnes, 75 mg and 610 °C.

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