WASC 2321

Overview of Stability Testing of Colloidal Propellant at DQA/TS Bishopton

AN OVERVIEW OF STABILITY TESTING OF COLLOIDAL PROPELLANT AT DQA/TS, BISHOPTON.

Colloidal propellants are essentially propellants based on nitrocellulose. They may contain other nitrate esters such as nitroglycerine, plasticisers and ballistic modifiers. Nitrate esters, unlike nitramines and aromatic nitro-compounds, decompose spontaneously and consequently propellant containing these materials must be stabilised. The type of stabiliser used depends on the chemical composition of the propellant and/or its end use.

Since colloidal propellants may decompose significantly even at normal storage temperatures, test procedures must be applied to ensure that the propellant is safe.

For Quality Assurance purposes there are two aspects in assessing stability.

1. A rapid test to ensure that the material is safe for further processing, filling, transporting or storage.

2. More lengthy tests for life-assessment or to confirm stability.

The safe-life of propellant is often taken as the time for the stabiliser content to fall to ½ of its original value. In the majority of stability tests, the ageing of propellant is accelerated by heating prepared samples at elevated temperatures. The decomposition so produced is related to an equivalent number of years storage at ambient temperatures by assuming an increase in the rate of decomposition by a factor of approximately 3 for each 10°C rise in temperature.

The decomposition mechanism is not fully understood but the decomposition of nitrate esters is believed to be initiated by the following reaction:

$$RONO_2 \dashrightarrow RO^{\cdot} + NO_2 \quad \text{(figure 1)}$$

This step is then followed by a number of complex reactions whereby NO_2, NO CO and CO_2 are formed, and in the presence of stabiliser N_2 is also produced. Traces of nitrous and nitric acids are also formed through the reaction of the oxides of nitrogen with water present in the matrix, and these in turn catalyse and hence accelerate the decomposition process.

Stabilisers are added to propellant to react with the oxides of nitrogen and their acids, so that they are removed from the system before auto-catalysis can take place. However even in the presence of stabiliser, slow decomposition continues to take place with depletion of the stabiliser. When properly stabilised, propellant can be safely stored for many years (>30 years for gun propellant).

An Overview of Stability Testing of
Colloidal Propellant at DQA/TS, Bishopton.

The propellant matrix has a colloidal gel structure and behaves in many respects like a thermoplastic. When propellant ages the following events take place concurrently.

1. Decomposition of nitrate esters.
2. Formation of NO_2 and NO.
3. Reaction of NO and NO_2 with nitrate esters and water to form CO, CO_2, HNO_3 (and N_2).
4. Dissolution of gases in the matrix.
5. Diffusion of gases through the matrix.
6. Reaction of oxides of nitrogen and their acids with stabiliser.
7. Depletion of stabiliser.
8. Formation of stabiliser degradation products.
9. Evolution of heat.
10. Deterioration of performance and mechanical properties.

The size and shape of a propellant sample, its chemical composition, its environment and the temperature at which the tests are carried out will affect the outcome of a stability test.

With large samples the rate of formation of gases can be greater than the rate at which they can diffuse out of the sample, and in this case gases will accumulate in the matrix. If the pressure builds up until it exceeds the tensile strength of the propellant, cracks or voids will be formed. Oxides of nitrogen retained in the matrix will also react with the stabiliser.

With small samples gases will diffuse out of the matrix faster than they are generated, so there is no cracking.

In the case of short term tests (heat test and NO_x analysis) there is little reaction of NO_x with the stabiliser. For longer term tests there is back diffusion of the oxides of nitrogen into the propellant and these gases then react further with the stabiliser and nitric esters.

A number of stability tests have been devised to assess the stability of propellant compositions. These tests involve heating the propellant at an elevated temperature for a specified time and observing one of the changes indicated above.

An Overview of Stability Testing of Colloidal Propellant at DQA/TS, Bishopton.

(1) DETECTION OF EVOLVED OXIDES OF NITROGEN.

(a) The traditional tests are based on the time taken to produce a characteristic change in a reagent paper suspended in the sample tube. e.g. The Abel Heat Test where the oxides of nitrogen produce a brown line on starch/potassium iodide paper (figure 2). Duration of test about ½ hour. Sample size 1.6g ground to 1.0-2.0mm. A typical specification is not less than 10 minutes for a test temperature of 150°F.

A further example is the American Methyl Violet Test which is carried out at 134.5°C for single base and 120°C for double base propellant.

(b) NO_x Analyser (built at RARDE, Waltham Abbey) is currently being used to carry out more fundamental studies of this process. This equipment allows the continuous monitoring of the rate of evolution of NO and NO_2 from a heated sample. The output trace distinguishes between the initial decomposition of nitrosamines and the steady decomposition of nitrate ester.

In these two tests the oxides of nitrogen are displaced from the propellant before they can react further.

(c) Bergman - Junk Test is applied in certain countries to stability testing of propellant. For single base propellant the sample is heated at 132°C for 5 hours and the evolved oxides of nitrogen are dissolved in a water trap. The resultant acid in the water trap is subsequently titrated with standard sodium hydroxide solution.

In the UK this test is only applied to the stability testing of nitrocellulose, where the specification limits are 1.2 mg/g nitrogen.

(2) MONITORING LOSS IN WEIGHT.

The loss in weight on prolonged heating is used as an indication of the degree of chemical breakdown in the propellant.

(a) The Dutch Test (figure 3). The sample is heated at 105 or 110°C for 72 hours and the loss in weight monitored. A typical specification is not more than one percent weight loss over the period 8 to 72 hours. Sample size 4.0g ground to 2.8 to 4.75mm.

(b) The 90°C Test is an attractive alternative as it can give additional information. Similar apparatus is used, the loss in weight is plotted and the inflection point between steady weight loss and exponential decomposition is noted. The specification requires that there is not more than 3% weight loss after 18 days. A disadvantage of the method is that it has a duration of some 3 weeks.

(c) The Small Vessel Test, which involves heating the propellant for 5 days at 100°C in a vented tube, is used for small arms propellant.

(3) MEASUREMENT OF SELF HEATING

(a) Silvered Vessel Test (figure 4)

The propellant is heated at 80°C in a Dewar distillation flask and the time taken for the propellant temperature to rise 2°C (or for fumes of NO_2 to be observed) is noted. This test is used in the stability area to assess the safe-life of new propellant composition. It is also used extensively in compatibility testing.

The duration of the test can be about 3 months. Sample size 8 ounces ground to 1.0 - 2.0mm.

(b) Micro Heat Flow Calorimeter.

The propellant is heated isothermally at 80°C and the differential output in microwatts is monitored. At one time it was considered that this test would replace the silvered vessel test. This has certainly not happened in the UK and the test is used at present to accumulate data for comparative purposes. Possible advantages of this test is a reduced analysis time of 1 or 2 weeks and greater safety in operation. Sample size is 2 ounces ground to 1.0 - 2.0 mm.

(4) DETERMINATION OF STABILISER CONSUMPTION.

In this type of test the propellant is heated at a prescribed temperature for a fixed period of time. The stabiliser content before and after heating is determined by gas chromatography and the fall in stabiliser content is calculated.

(a) The most widely accepted test is the NATO test which is carried out at 65.5°C. Duration of test 60 or 120 days: Sample size 20g - Minimum size $\frac{1}{8}$ cm^3. This test is currently applied only to diphenylamine and carbamite stabilised propellants and has the advantage that the procedure gives prescribed criteria for extending the life of propellant for a further period of 5 or 10 years storage. However it is open to question if this interpretation of results can be applied universally to the full range of propellant compositions.

At present there is no such widely accepted criteria for life-extension of propellants stabilised with 2-nitrodiphenylamine and p-nitro N-methylaniline.

(b) The Woolwich Test is applied to small arms propellant and the sample is heated at 80°C in an atmosphere of 95% relative humidity for 3 weeks. The requirement of the test is that the stabiliser (diphenylamine) shall not fall to less than $\frac{1}{4}$ of its original value.

(5) DETERMINATION OF STABILISER DEGRADATION PRODUCTS

In Germany the diphenylamine stabiliser degradation products are determined quantitatively by a thin lay chromatographic procedure.

Modern requirements in the UK for assessing Ordnance Board Trials or shelf-life of propellants withdrawn from service make it necessary to determine the nature and amounts of stabiliser degradation products present in the aged propellant. Liquid chromatography (HPLC) is used extensively in the quantitative analysis of stabilisers and their degradation products. (figure 5).

The early appearance of trace amounts of a particular degradation product may give an early indication of propellant instability. It is easier to resolve changes of 0.01 percent at trace level than at the 7 percent level where the precision of the method may be ± 0.05 percent.

Procedures based on measuring trace levels of degradation products may find application in accelerated ageing at 50°C for several weeks instead of the customary 6 months to one year required for this low temperature.

The nature of the degradation products in the case of carbamite, is highly dependent on the temperature (figure 6). Low temperatures favour the formation of nitrosamines by direct reaction of nitroglycerine with carbamite, while high temperatures favour the reaction of oxides of nitrogen with carbamite to form nitrocentralites. Some of these degradation products may be stabilisers in their own right.

(6) ASSESSMENT OF GASSING IN PROPELLANT.

(a) 2" cube crack test

A 2" cube of propellant is heated at 80°C and x-rayed every 2 days until there is evidence of porosity or cracking. Duration of test is 2 or 3 weeks.

(b) Vacuum Stability Test.

5.0g of propellant chopped to a size of $^1/_8$ cm^3 is heated in an evacuated test tube at 80°C for one week (fig.7) and the total volume of gases evolved is measured (typically 1 to 2 mls total volume).

The equipment used includes Druck pressure transducers, a Hewlett Packard Data Acquisition unit and an HP85 computer.

At the end of the run a graph of volume against time on scaled axis is plotted on an HP7470 plotter (fig. 9).

The headspace gases are subsequently sampled and analysed on an HP5880 gas chromatograph (fig. 9)

The above test is also used for compatibility testing of propellant.

(7) SURVEILLANCE OF BULK STORED PROPELLANT (EXAMINATION ORDERS)

Propellant is periodically withdrawn from magazines for examination to assure a further period of safe storage. The principal test used in this area is the Abel Heat Test. However since propellant with a satisfactory heat test may have a very low residual stabiliser content, and conversely propellant with a low heat test may have an adequate residual stabiliser content, the Colour Test is used to complement the heat test.

In the Colour Test the propellant is dissolved in acetone and the colour produced by the dissolved nitrosamines and nitro compounds are matched against standard colour tints. A low colour number indicates high stability.

This test is only applicable to carbamite stabilised propellants.

In conclusion it must be stressed that the decomposition reactions occurring at elevated temperatures are unlikely to be the same as those occurring in propellant at normal ambient temperatures. Also the preparation of the sample for analysis (i.e. the size to which it is reduced) and its environment (i.e. the availability of air and moisture) will affect the decomposition reactions.

It is always advisable therefore to use more than one test to assess the stability of propellant. The two tests most widely used by DQA/TS are the Abel Heat Test for rapid assessment of stability and the NATO test for confirmation of stability and life-assessment.

P.

Stability testing of colloidal propellant is largely traditional or empirical. However there is a growing requirement to more fully understand the decomposition of propellant with a view to predicting the stability and shelf life of modern propellant compositions. Liquid and gas chromatography, infrared and mass spectrometry are extensively used in this field.

Most of the work in the area of life-assessment has been confined to propellant stabilised with diphenylamine and carbamite. However as 2 nitrodiphenylamine and p nitro N methylaniline stabilised compositions progressively "come of age" similar methods for life assessment will require to be formally introduced.

An Overview of Stability Testing of
Colloidal Propellant at DQA/TS, Bishopton.

A considerable amount of work has been carried out at RARDE (Waltham Abbey) in studying the kinetics of propellant decomposition using a variety of instrumental techniques. DQA/TS, Bishopton are currently trying to adapt a number of these techniques for Quality Assurance purposes e.g. NO_x Analyser, Vacuum Stability, Micro Heat Flow Calorimeter and Thermal Analysis.

DECOMPOSITION OF NITRATE ESTERS

$$RONO_2 = RO\cdot + NO_2$$

$$RO\cdot = R'\cdot + CH_2O$$

$$2CH_2O + 3NO_2 = 3NO + 2H_2O + CO + CO_2$$

$$(2R\cdot) + 7NO_2 = 7NO + 3H_2O + 2CO_2$$

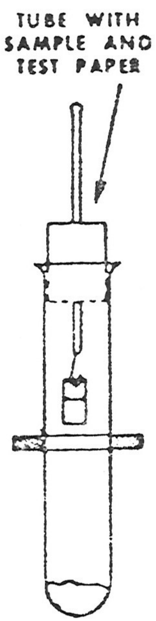
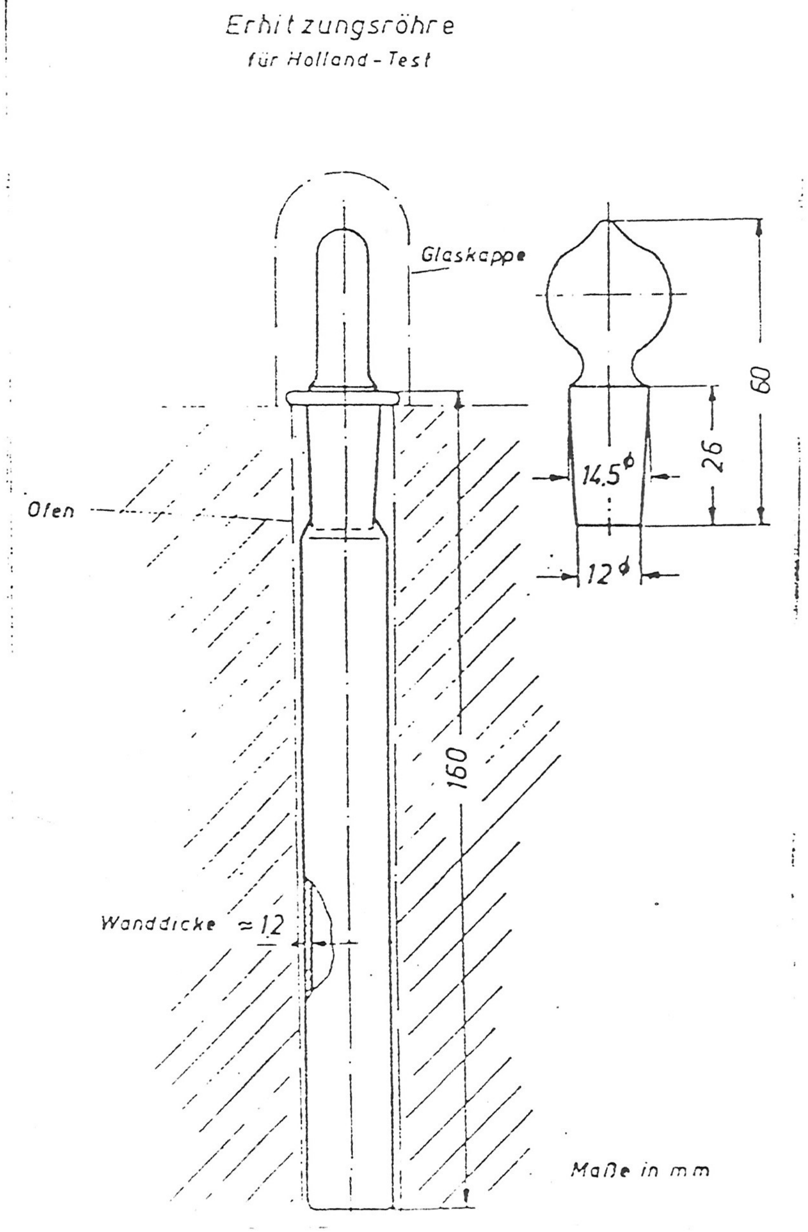


Fig. 1 Apparatus for Abel's Heat Test



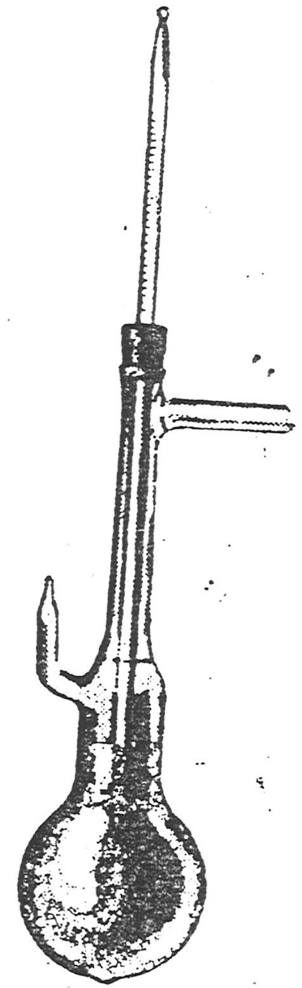
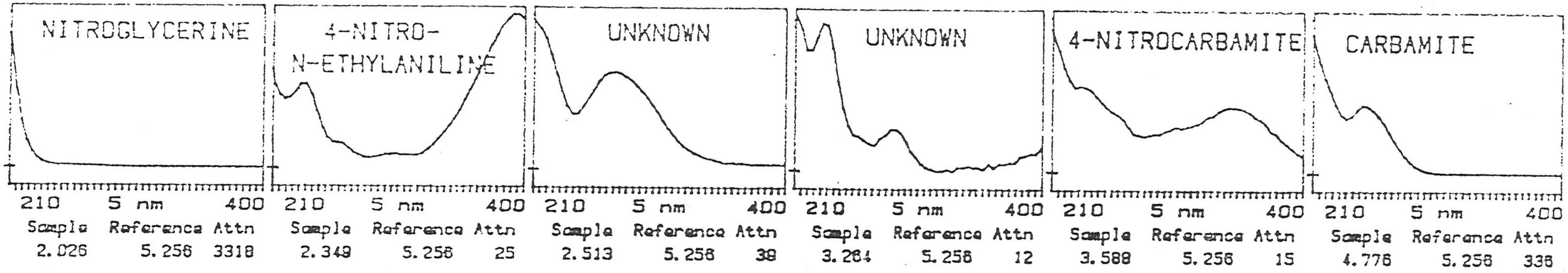
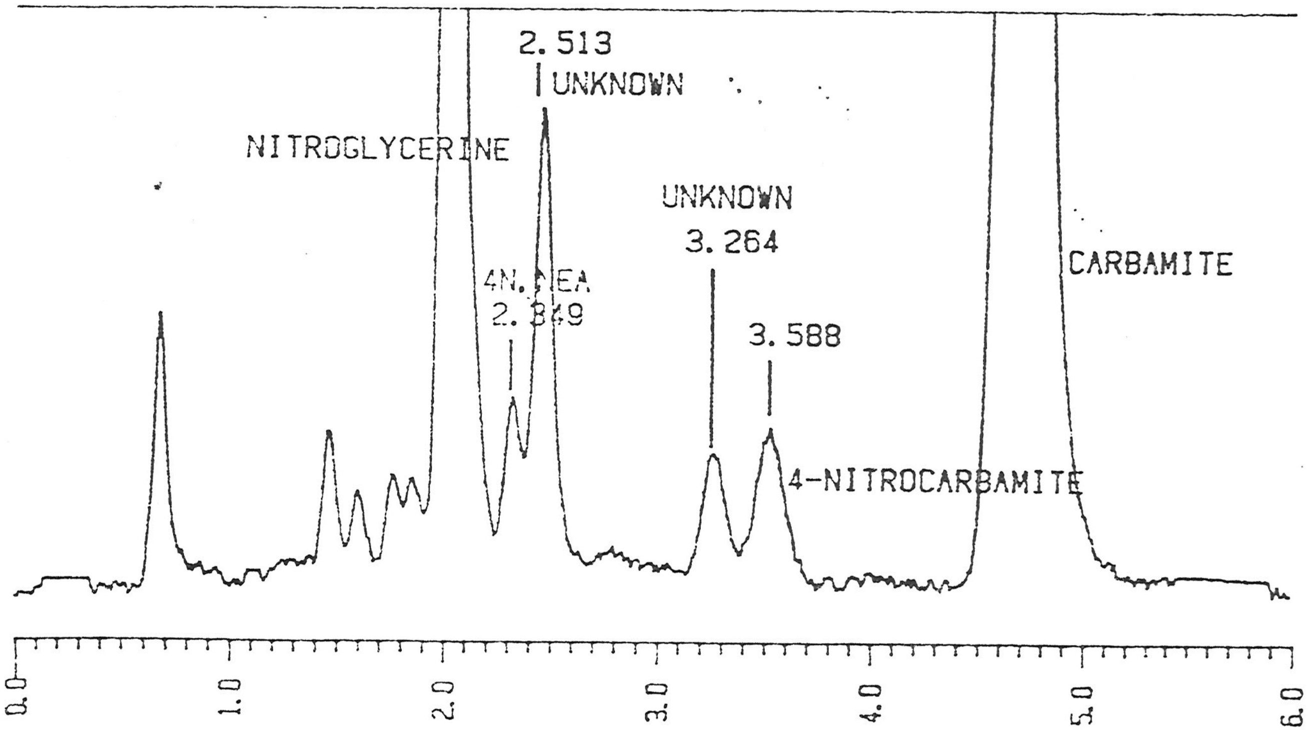


Fig. 2 Silvered vessel apparatus

File: GRW001 hp 1040A

Date: 05/03/1984 AGED PROP. SC/Z (30 DAYS 80 C)





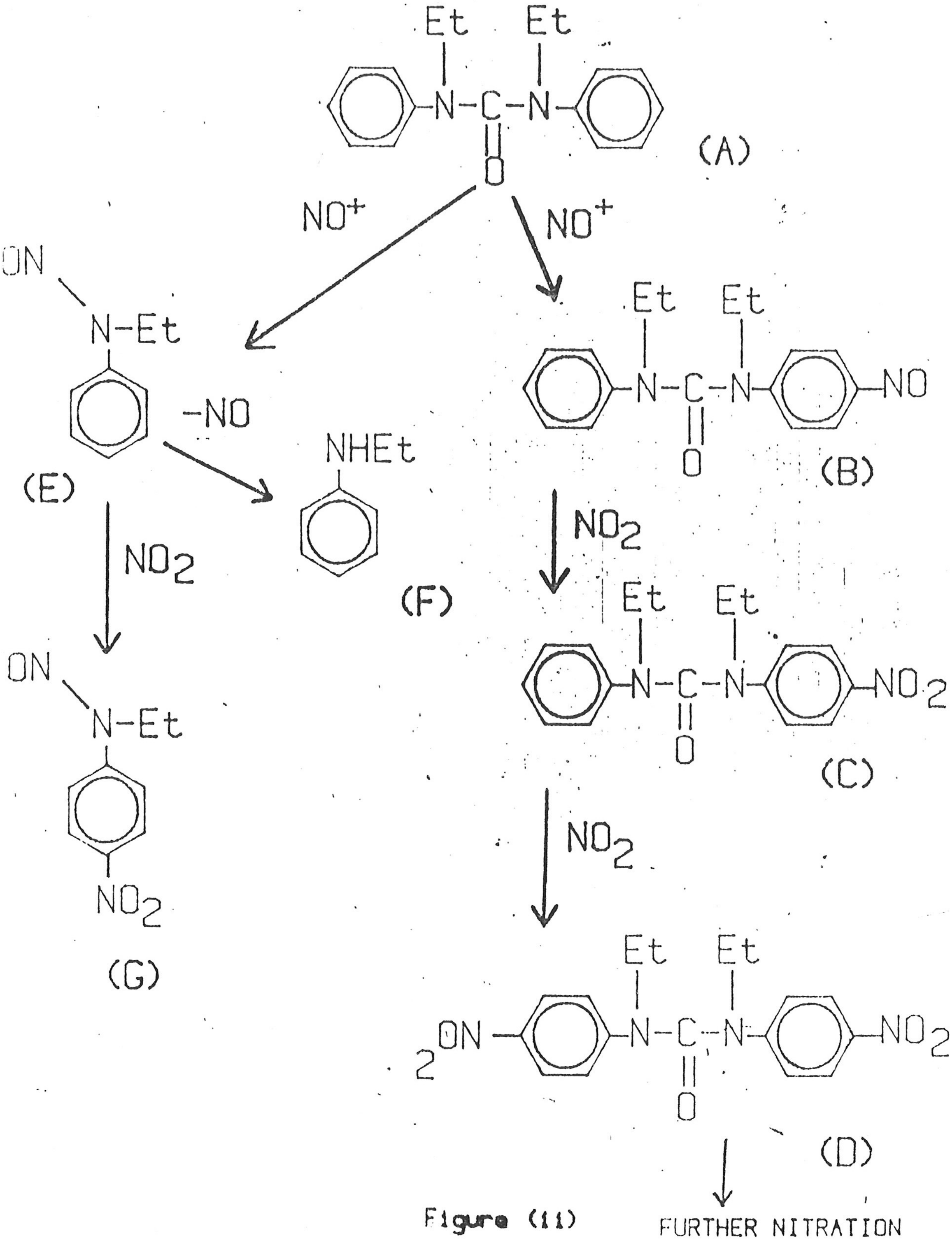
Inj. Time: 09:41

Attn [mAU]: 50.0 (213.3)

Zero%: 10%

Signal: A: 2,8 Set

Wavelength:
1 . 210, 4
2 . 230, 4
3 . 254, 4
4 . 260, 80
5 . 280, 4
6 . 320, 20
7 . 450, 50
8 . 550, 100



Et
Et
(A)
NO+
NO+
ON
N-Et
-NO
NHEt
(E)
(F)
NO2
ON
N-Et
NO2
(G)
Et
Et
NO
(B)
NO2
Et
Et
NO2
(C)
NO2
Et
Et
O2N
NO2
(D)
FURTHER NITRATION

Figure (ii)

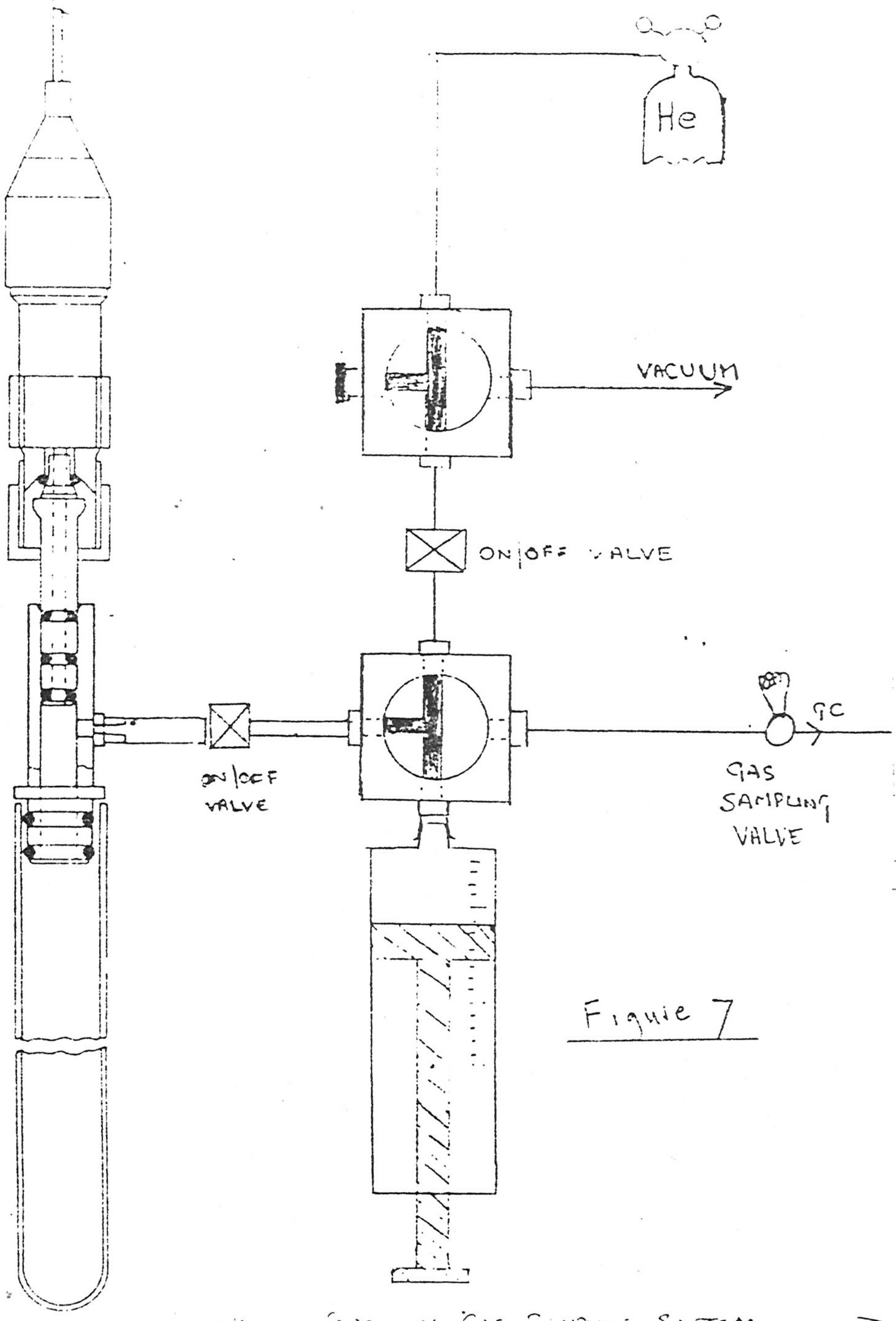


Figure 7

Figure 8

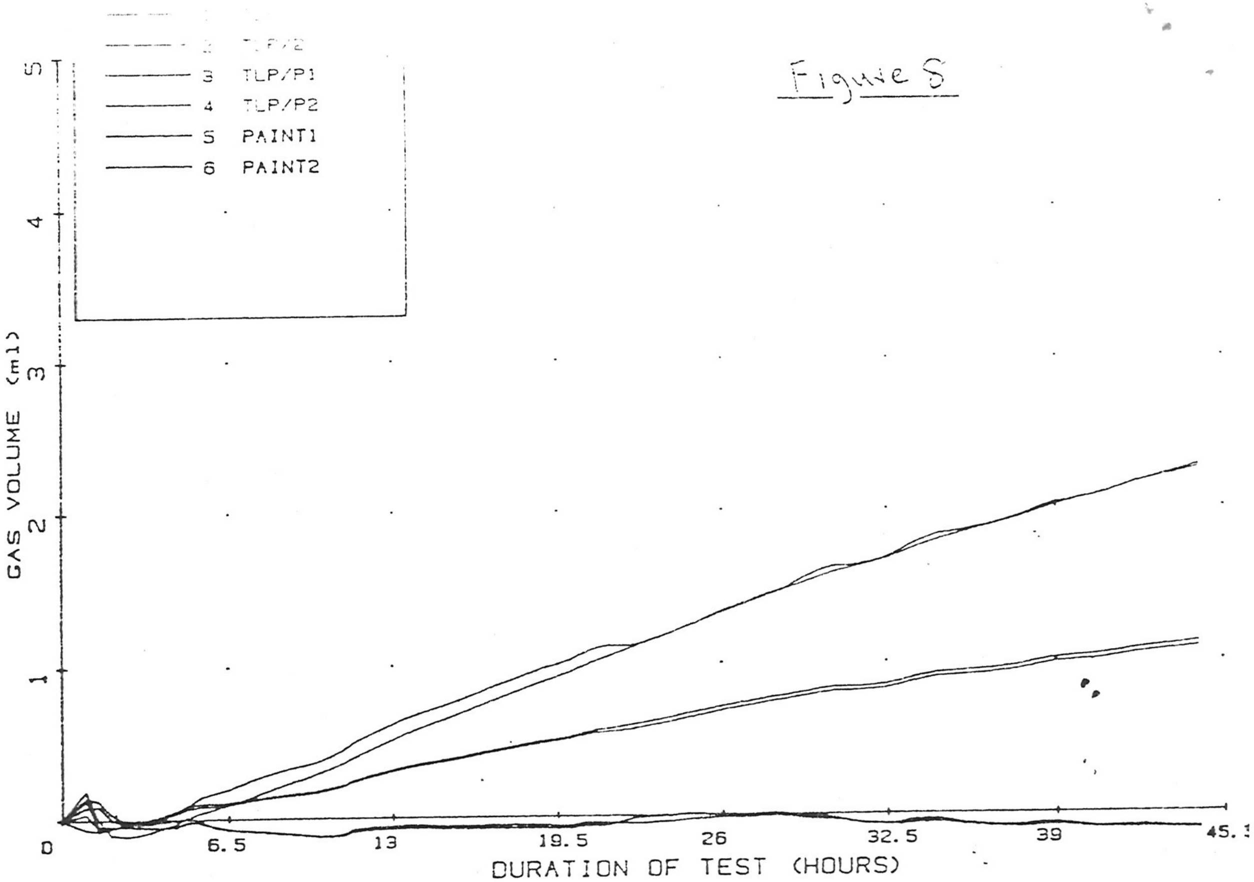


Figure 9