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USE OF THE 'MARKHAM' SEMI-MICRO STILL FOR THE DETERMINATION OF --ETC(U)
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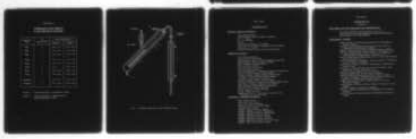

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USE OF THE "MARKHAM" SEMI-MICRO STILL FOR THE DETERMINATION OF STABILISERS IN PROPELLANTS

PART 1: DETERMINATION OF ETHYL CENTRALITE AT THE 3-8% LEVEL

R.G. Davidson

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PART 1. DETERMINATION OF ETHYL CENTRALITE AT THE 3-8% LEVEL.

(10) R.G. Davidson

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ABSTRACT

The use of the 'Markham' semi-micro still in the determination of ethyl centralite in propellants is described. The new procedure gives results which compare well with those from the traditional steam distillation-gravimetric method, so that continuity can be ensured for propellants undergoing extended accelerated thermal ageing. A determination can be completed within thirty minutes by the new method, compared with 24 hours by the existing method. The apparatus is more compact, and smaller amounts of sample and reagents are required. The ethyl centralite is determined by direct spectrophotometry of the steam distillate, thus eliminating solvent extraction and subsequent chemical operations involved in the gravimetric method.

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16. ABSTRACT (if this is security classified, the announcement of this report will be similarly classified):

Steam distillation of ethyl centralite from propellants has been achieved on a semi-micro scale by the use of the "Markham" semi-micro still. The ethyl centralite so separated is determined by direct spectrophotometry of the distillate. The results for a range of double and triple base propellants that contain 3-7% ethyl centralite agree well with those from the traditional steam distillation/gravimetric method. The semi-micro procedure is simpler and much quicker than the traditional method, and is applicable to both new and aged propellant.

CONTENTS

USE OF THE "MARKHAM" SEMI-MICRO STILL FOR THE DETERMINATION OF STABILISERS IN PROPELLANTS

PART 1: DETERMINATION OF ETHYL CENTRALITE AT THE 3-7% LEVEL

1. INTRODUCTION

The long-term stability of propellants manufactured in Australia is assessed by accelerated thermal ageing at 49°C (dry). The stabiliser content is determined and the Abel heat test (1) is applied at yearly intervals up to a maximum of five years. The results are used to predict the safe service life of the propellant under normal storage conditions. At these laboratories, the standard method for the determination of stabiliser in propellant has always been separation of the stabiliser by steam distillation, followed by bromination; the analysis is completed gravimetrically (2). The procedure is tedious and time consuming and a more rapid method of analysis is desirable to conserve laboratory resources. However, the body of knowledge and experience in assessing long-term stability of propellant in Australia is based on the use of the steam distillation method. Thus, a change to a more modern procedure such as thin layer chromatography, gas-liquid chromatography or high pressure liquid chromatography would involve a considerable programme of work to correlate the results given by different methods so that continuity could be assured for propellants already undergoing accelerated thermal ageing.

This report sets out the results of the first stage of a programme of work aimed at simplifying and shortening the determination of stabilisers in a variety of propellants by the steam distillation method. The propellants selected for this investigation were a group of double and triple base propellants which contain between three and seven per cent ethyl centralite (EC) as a stabiliser and solid plasticiser.

In the current method used at these laboratories (2) the propellant is decomposed with ethanolic alkali and the solution is steam distilled. EC is extracted from the distillate with diethyl ether and converted to the dibromo compound with bromine. Excess bromine is destroyed with gaseous

sulphur dioxide and the diethyl ether is evaporated with a current of air. The residue of dibromoethylcentralite is dissolved in a little hot ethanol and reprecipitated with water. The precipitate is allowed to stand overnight, it is then filtered, dried and weighed. The usual sample size is 3-5 g; the distillation is carried out from 1 litre flasks and takes 1-1.5 hours. Each analysis requires about 200-250 cm^3 of diethyl ether. For routine purposes, the analysis of a number of samples occupies considerable time and space, and large volumes of solvent are required. There are a number of points in the analysis at which improvements could be effected :

1. The lengthy distillation step could be shortened by reducing the sample size, and this would also enable smaller apparatus and reagent volumes to be used.

2. The extraction step could be either modified by substitution of a non-flammable solvent (for example dichloromethane) or, preferably, eliminated altogether.

3. The tedious, time-consuming and somewhat hazardous steps from the bromination procedure onwards could be replaced by a simpler, more modern measurement technique such as absorption spectrophotometry (3).

Early work with the spectrophotometric evaluation of steam distillates did not yield very concordant results between laboratories (4) but the method was subsequently incorporated in MIL-STD-286B (5). However, since spectrophotometry is by far the simplest method of determining EC in solution, that technique was selected for the initial investigations.

2. EXPERIMENTAL

2.1 Propellants

2.1.1 Composition

The nominal composition of the propellants used in this work are as follows :

TYPE / INGREDIENT	A NQ	B MNQF	C MNF2P	D MECHANITE
Nitrocellulose, %	20.8	21.0	16.5	50.4
Nitroglycerine, %	20.6	21.0	21.0	34.9
Picrite (1-nitroguanidine)	55.0	55.0	55.0	-
Di-n-butylphthalate, %	-	-	-	8.1
Ethyl Centralite,* %	3.6	3.0	7.5	6.6

* 1,3-diethyl-1,3-diphenyl urea

2.1.2 Sample Preparation

Propellants in the form of rods or slotted tube (A, B & C) were ground in a cup and cone type mill (6) to a particle size between 1 mm and 2 mm. Propellant D is in the form of a cylindrical extrusion approx. 10 cm diameter, and samples from this form of propellant were obtained either by drilling, or by removing slices from the face of the cylinder, followed by size reduction in the cup and cone mill.

2.2 Reagents

Sodium hydroxide, "Analar", and ethanol, absolute, were used as received. Distilled water was used throughout.

2.3 Apparatus

The "Markham" semi-micro still unit ("Quickfit" Catalogue No. MC 46) is shown in Fig. 1. The basic features of the unit are an inner distillation chamber A, surrounded by a concentric jacket B; the connection between the two is via the steam inlet tube C. Steam enters the apparatus at D, heats the outer jacket, passes into the inner chamber and leaves via the splash trap E and the condenser F. A waste outlet G may be used to control the amount of steam passing into the inner chamber. The sample and any reagents are added through the inlet point H. To empty the apparatus at the end of a determination, the steam is shut off and the waste outlet is closed. Cooling reduces the pressure in the outer jacket which causes the contents of the inner chamber to be sucked into the jacket via the steam inlet tube C. The inner chamber is then rinsed and is ready for the next sample. The jacket is emptied via the waste outlet G.

Steam may be provided by a conventional steam generator, or by a line supply. To avoid pressure fluctuations and the need to refill a boiling water reservoir, a continuous steam generator ("Büchi", model 1500) was used. The unit will provide steam within 1-2 minutes of switching on, and has ample capacity to operate two "Markham" still units simultaneously. Steam is supplied at a constant static head of about 50 cm of water; it is impossible to achieve a dangerous pressure buildup in the system, as any increase in pressure pushes the water away from the electrodes and steam generation ceases.

2.4 Distillation Conditions

The traditional steam distillation procedure requires a 3 g sample of propellant and 125 cm^3 of ethanolic sodium hydroxide. The optimum volume for the "Markham" still is about 15 cm^3, and this suggested a sample mass of 0.3 g to maintain sample/reagent relativities. The initial difficulty lay in transferring the sample quantitatively into the distillation chamber. Particles of propellant tended to stick to the sides of the inlet point below the stopper, and could not be rinsed in by water, ethanol or ethanolic sodium hydroxide reagent. Another problem was that unless adequate steam was flowing when the reagent was added, the contents of the reaction chamber were sucked into the jacket due to local cooling, and if enough steam was flowing to avoid "suckback" the reaction between the propellant and the reagent was so vigorous as to be uncontrollable and "boil over" was the result.

These problems were all overcome by solution of the sample in ethanolic sodium hydroxide, and transfer of the solution to the apparatus with enough steam flowing to prevent "suckback". The concentrations of ethanol and sodium hydroxide in the solution used to dissolve the propellant were selected so as to achieve rapid solution without the reaction becoming too vigorous. It was found that the rate of solution of the propellant was much more sensitive to ethanol concentration than to sodium hydroxide concentration, and the latter was set at 20% $^{m}/v$ to give the same level, after dilution in the apparatus, as in the traditional method. It is necessary to use heat to dissolve the samples; if the ethanol level is much above 20% $^{v}/v$, a vigorous exothermic reaction occurs after a brief induction period, and EC may be lost by volatilisation. If the ethanol concentration is much below 20% $^{v}/v$ the reaction is relatively slow, and the solution may be inadvertently overheated, again with the possible loss of EC. The recommended concentrations give a rapid, easily controlled solution of all the propellants tested, though the different formulations and physical forms reacted somewhat differently.

Operation of the still is relatively straightforward, but care must be exercised when adding samples or solvents via the inlet point when steam is flowing. The rate of addition must be slow enough to maintain distillation during the addition so as to avoid "suckback" or superheating and unstable distillation conditions. Controlled addition is not difficult to achieve in practice.

The connections between the steam generator and the still should be of glass and silicone rubber. Flexible PVC or rubber tubing should not be used as they contain compounds which absorb in the ultraviolet region; these may be leached by the steam and will interfere in the subsequent spectrophotometric measurements.

2.4.1 Establishment of Distillation Volume

To determine when all the EC had distilled, the spectra of successive 10 cm^3 fractions of the distillate from a number of samples were recorded over the range 210-300 nm.

2.4.2 Analysis of Distillates

The distillates were examined to determine whether any EC degradation product or other compound had distilled that might interfere in the analyses. Ultraviolet spectra of distillates were recorded on a Varian model 635 spectrophotometer between 210 nm and 300 nm. The solutions were then diluted with water and extracted with dichloromethane. The extracts were analysed by thin layer chromatography on 0.25 mm layers of silica gel GF254 (Merck). Petroleum spirit (40^{o}-60^{o})/methanol (95 + 5) was used as the eluant, and the developed plates were evaluated by examination under ultraviolet light (254 nm) and by exposure to iodine vapour.

2.5 Procedure for the Analysis of Propellant

Dissolve a suitable mass of sample (Note 1) in 10 cm^3 of ethanolic sodium hydroxide (20% $^m/_v$ in 20% $^v/_v$ ethanol) in a 50 cm^3 beaker with gentle heating. Pass steam through the "Markham" still unit for a few minutes to achieve stable operating conditions, then transfer the sample solution to the cup H, with the stopper in place. Adjust the steam flow to give 3-4 cm^3/minute of condensate, place a 100 cm^3 volumetric flask under the outlet of the condenser, then loosen the stopper and allow the sample to enter the apparatus, taking care to maintain a liquid seal around the stopper at all times. Rinse the beaker with 5 cm^3 of water, then with 5 cm^3 of ethanol, add the rinsings to the cup, loosen the stopper, transfer the rinsings to the distillation chamber, close the stopper and add 20 cm^3 of ethanol to the cup. Increase the steam flow to give about 5 cm^3/minute condensate and distil until about 60 cm^3 of distillate have been collected. Loosen the stopper and allow the ethanol to flow into the apparatus slowly so that the distillation continuous smoothly.

When all the ethanol has distilled, close the waste outlet, shut off the steam and wash out the inner chamber with distilled water. Open the waste outlet, turn on the steam again and the apparatus is ready for the next analysis.

Thoroughly mix the contents of the volumetric flask, dilute to the mark with water and measure the absorbance at 247 nm in a 1 mm cell against a reference solution prepared by a distillation in the absence of propellant. Calculate the ethyl centralite content of the propellant as follows :

$$\text{ethyl centralite, \%} = \frac{A \times 1000}{K \times m \times 1}$$

where A = absorbance of sample at 247 nm

K = absorption coefficient of ethyl centralite in 30% $^v/_v$ ethanol, at 247 nm, litres per g.cm

m = mass of sample, g

1 = path length of cell, cm

Note 1. Sample mass required for various ethyl centralite contents.

ethyl centralite, %	sample mass, mg
1-5	300 ± 0.3
5-8	200 ± 0.2

3. RESULTS AND DISCUSSION

Analysis of successive 10 cm^3 fractions of the distillate showed that in most cases all the EC was contained in the first 40 cm^3 of distillate. To allow a margin of safety, 60 cm^3 is collected in routine analysis.

The distillates from various samples were checked to determine whether any breakdown products distilled with the EC. The major breakdown products of EC are N-nitroso-N-ethylaniline and 4-nitroethylcentralite (7). Hydrolysis of these compounds produces N-ethylaniline and a mixture of N-ethylaniline and 4-nitro-N-ethylaniline respectively. The ultraviolet absorption spectra of the distillates were identical to that of pure EC distilled under the same conditions and the thin layer chromatogram of the dichloromethane extract of the distillate revealed only EC. The distillate from some old propellants showed traces of 4-nitro-N-ethylamiline. However as the amounts were small they did not significantly interfere with the analysis.

The results of analysis of a number of samples by the method described above are shown in Table 1. Also shown are the results of analysis of the same samples by the standard steam distillation method (2). Analysis of a wide range of samples in duplicate indicated that the reproducibility is about 0.04% absolute between duplicate analyses at the 7% EC level, and 0.02% absolute at the 3% EC level. The agreement between the two methods is quite adequate for the purposes of stabiliser monitoring.

4. CONCLUSIONS

The procedure described offers a useful alternative to the current method used to determine EC in both fresh and aged samples of the four types of propellant examined. The 'Markham' semi-micro still is compact and easily operated and the analysis procedure requires fewer operations and takes less time than the currently used method. A single sample can be analysed in about 30 minutes from a cold start, but in routine use and if two stills are used simultaneously some 40 determinations may be carried out in a normal working day. The results can be directly correlated with those obtained using the current method so that continuity is assured in the case of propellants already undergoing extended thermal ageing trials.

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TABLE 1

DETERMINATION OF ETHYL CENTRALITE IN AGED PROPELLANT BY TWO METHODS

Propellant Type	Age Years at 49°C	Ethyl Centralite, %	
		Method 1	Method 2
MNQF	2	2.79, 2.79	2.76, 2.78
MNQF	3	2.76, 2.72	2.76, 2.80
MNQF	4	2.61, 2.60	2.59, 2.61
MNF2P	0	7.23, 7.31	7.25, 7.28
MNF2P	1	7.24, 7.27	7.24, 7.21
MNF2P	2	7.33, -	7.24, 7.25
MNF2P	3	7.05, 7.02	6.98, 7.02
MNF2P	4	7.04, 6.88	6.90, 6.98
MECHANITE	0	6.99, 7.01	6.91, 6.87
MECHANITE	0	5.70, 5.69	5.60, 5.60

Method 1: Steam distillation - gravimetric finish

Method 2: Steam distillation - (Markham Still) - spectrophotometric finish

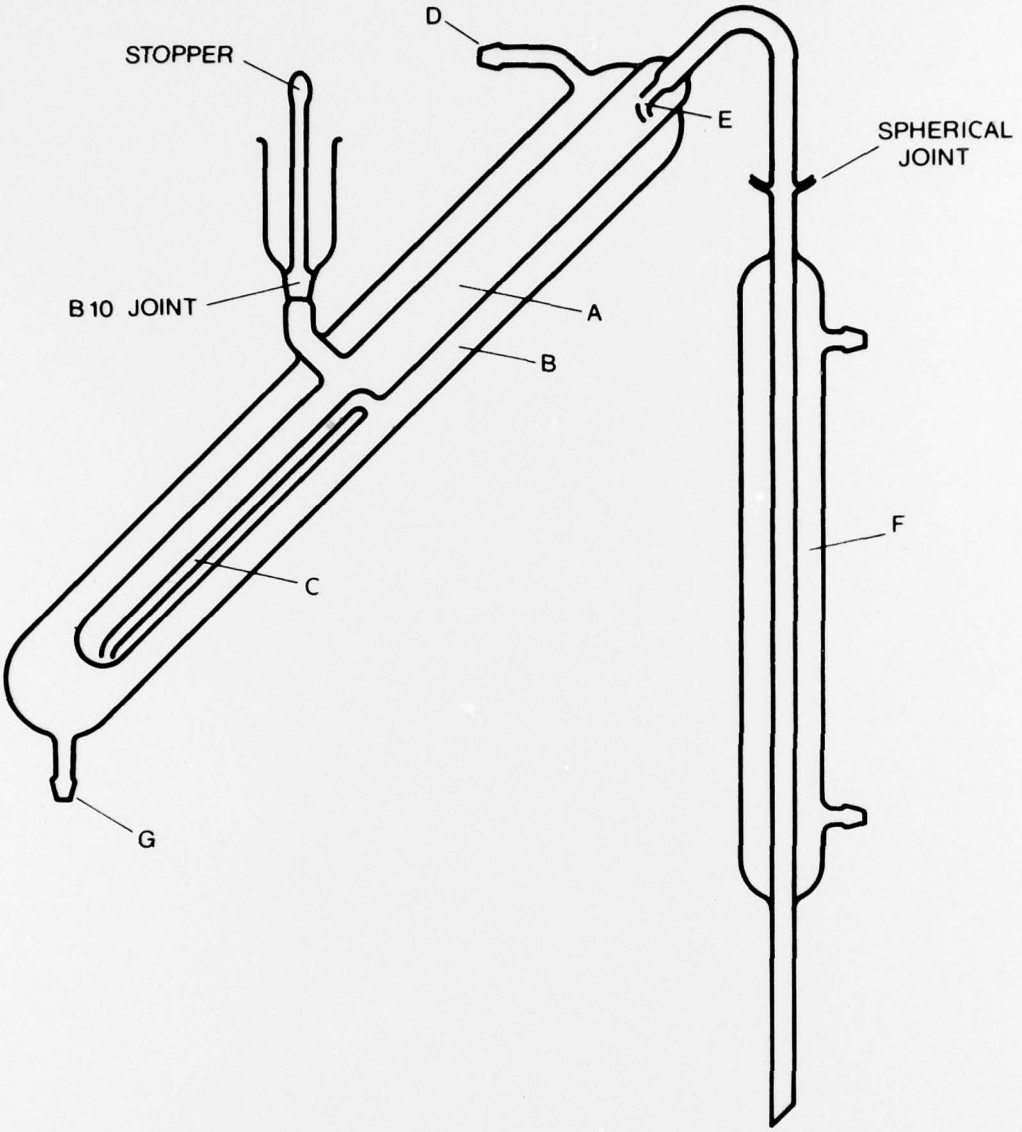

FIG. 1 - "Markham" semi-micro still "Quickfit" MC46.

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