Methylcentralite Concentration Profiles in Monoperforated Extruded Nitrocellulose and Nitrocellulose / Nitroglycerine Propellant Grains by Raman Microspectroscopy

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Synopsis

Raman microscopy was used to determine the methylcentralite (MC) concentration profiles diffused into single-base (nitrocellulose) (NC) and double-based (nitrocellulose/nitroglycerine) (NC/NG) small-arms propellant grains. External and internal concentration profiles were determined by measuring the concentration of MC relative to the NC and NC/NG at 5-μm intervals into the grain from the edge inward and the perforation edge outward. The external profile was constant with a diffusion and interaction mechanism, i.e., a level concentration of deterrent through the outer region of the grain followed by a gradual dropoff in concentration with distance into the grains, whereas the internal profile was found to be dependent on perforation size with either a diffusion and interaction mechanism profile or a gradual decrease in concentration profile.

INTRODUCTION

Deterrents (moderants) are materials that are diffused into single-based nitrocellulose (NC) and double-based nitrocellulose/nitroglycerine (NC/NG)

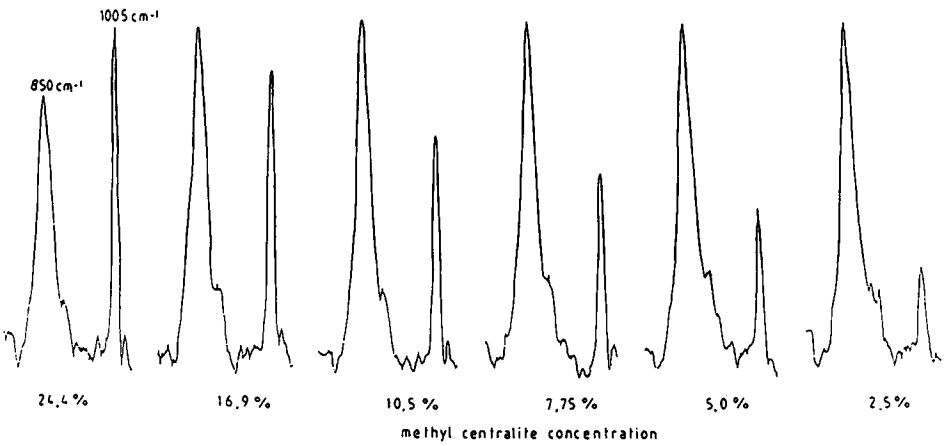

Fig. 1. Partial Raman spectra of calibration standards of % w/w methylcentralite/nitrocellulose.

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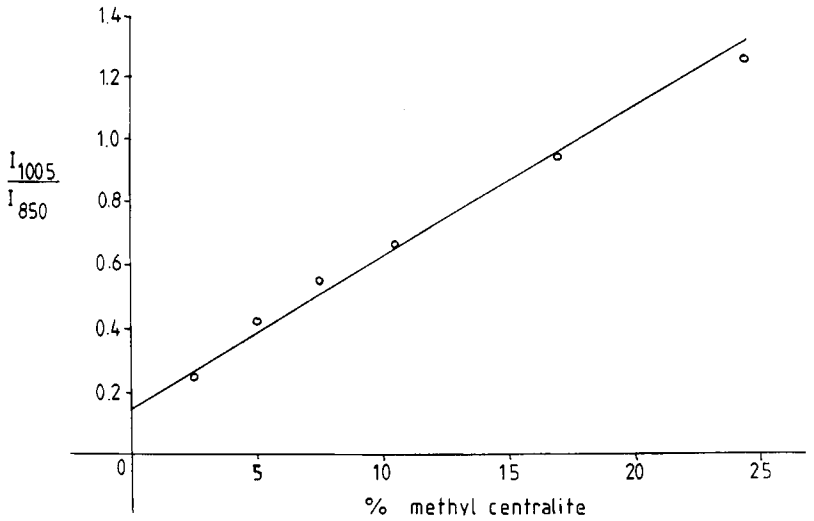


Fig. 2. Calibration graph of relative intensity I_{1005}/I_{850} vs. % w/w mehtyl centralite.

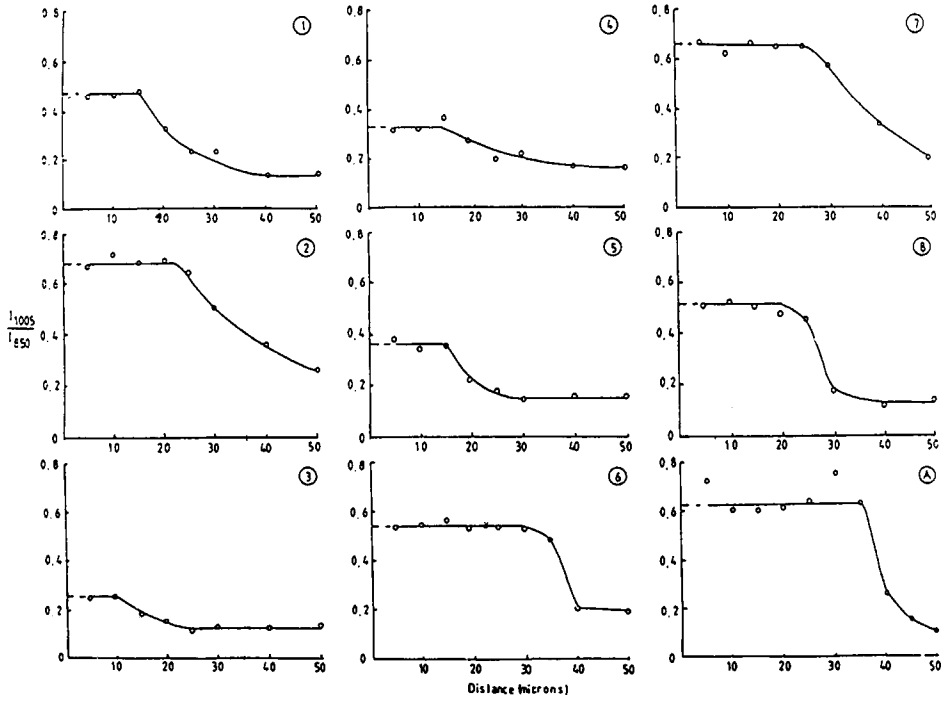


Fig. 3. External concentration profiles for nine different grains from the same batch.

small-arms propellant grains to modify the initial burning rate at the surface of the propellant and hence the rate of gas evolution. This avoids overpressure early in the ballistic cycle. Ballistic performance is thought to be related to the concentration and depth of penetration of the deterrent into the propellant grains. Hence the need for analytical methods for the qualitative and quantitative determination of the concentration and depth penetration profiles for the prediction of ballistic performance.

Established methods for measuring the penetration depth of moderants into nitrocellulose propellant grains include various staining and optical techniques;[1-4] however, these techniques were not directly capable of measuring the concentration profile of moderant in the grains. Until recently, to measure the concentration profile of the moderant required the use of specially prepared deterred propellants containing ^{14}C-radioisotope-labeled deterrents and autoradiographic,[5,6] and scintillation counting procedures. Recently we reported a laser Raman microspectroscopic method[8] for determining the qualitative concentration profile of methyl centralite in an extruded monoperforated nitrocellulose small-arms propellant grain which did not require specially prepared grains and used actual grains from a manufacturing run. An infrared microspectroscopy method has recently been reported.[9]

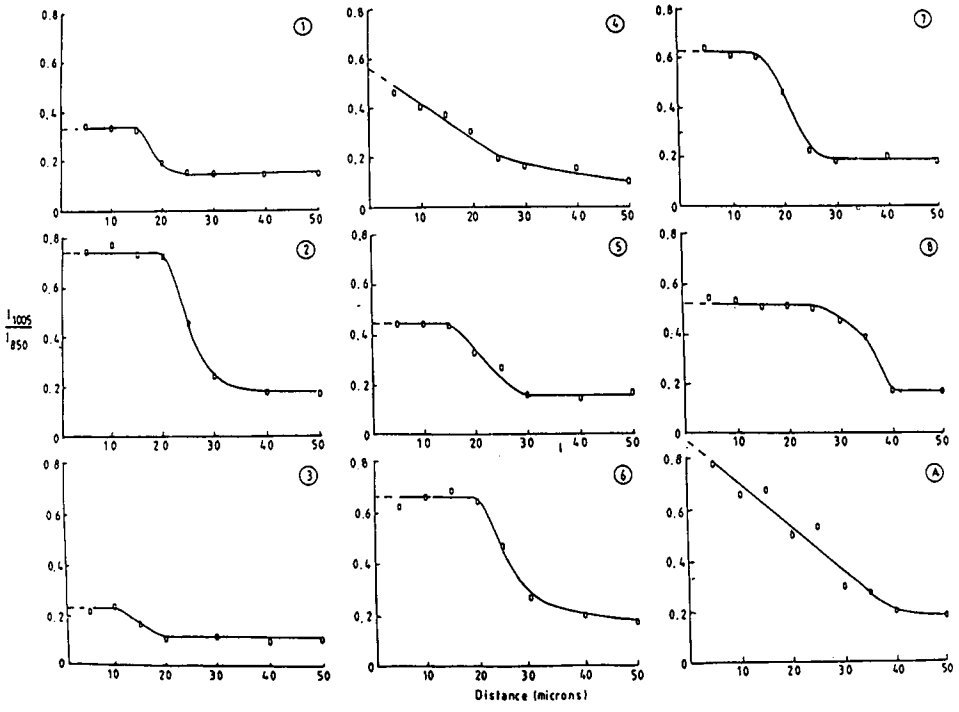


Fig. 4. Internal concentration profiles for nine different grains from the same batch.

In this communication we report on the quantitative concentration profiles obtained from several grains of MC/NC and MC/NC/NG extruded propellant grains, and the possible application of the Raman technique to other moderant systems.

EXPERIMENTAL

Propellant

The propellants used consisted of extruded monoperforated nitrocellulose base grains deterred with methylcentralite with nominal dimensions of 1.15

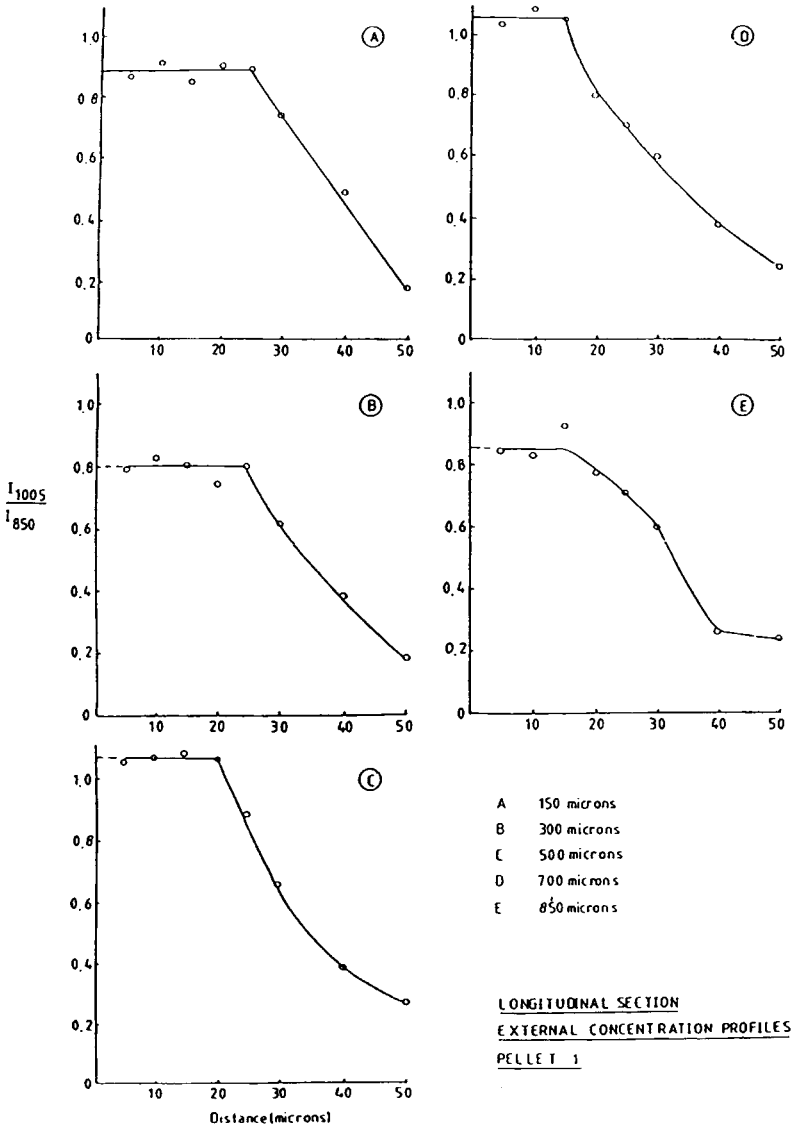


Fig. 5. Longitudinal section—external concentration profiles: (A) 150 μm; (B) 300 μm; (C) 500 μm; (D) 700 μm; (E) 850 μm.

mm, outside diameter 0.85 mm, and perforation diameter 0.17 mm, and NC/NG double-based grains containing 8% incorporated nitroglycerine and the same dimensions.

Microtomy

In our previous work 10-μm thick cross sections were used which were cut from the grains after embedding in an epoxy resin. For this work the method was modified to eliminate the epoxy, thus avoiding any spectral interferences from the embedding material. The modified method was to clamp the propellant grains into the microtome chuck and microtome the grains to approximately two-thirds of their original length and then the profiles were determined directly on the faced-off grains.

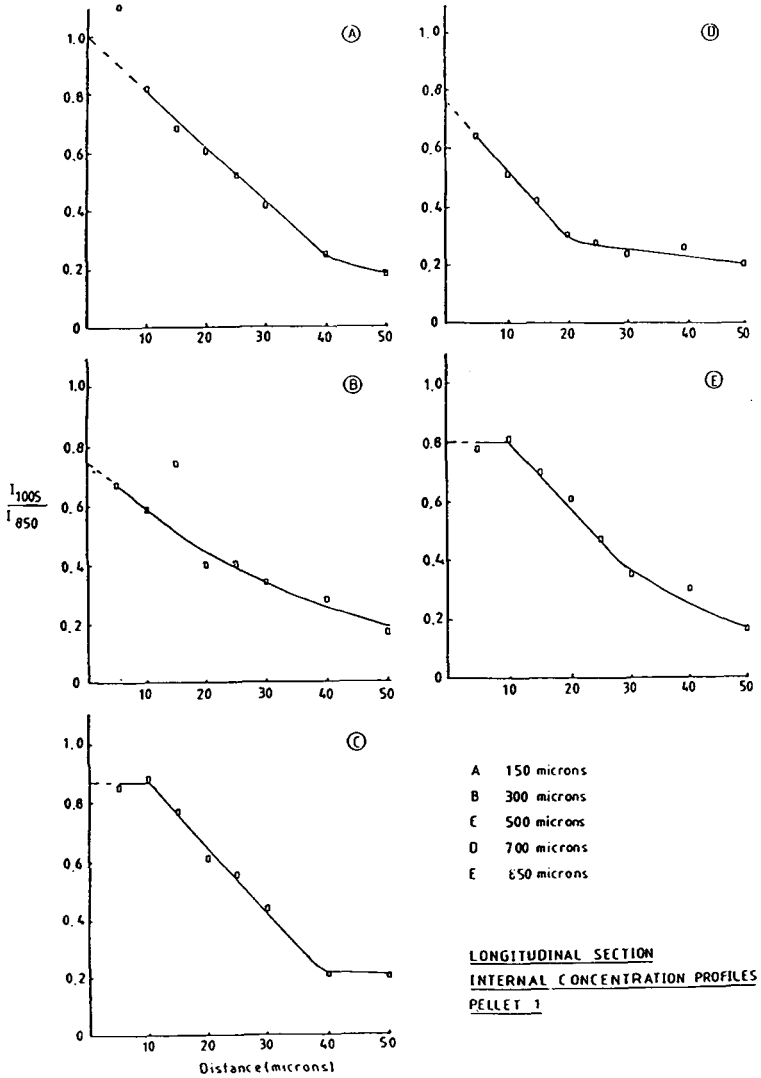


Fig. 6. Longitudinal section—internal concentration profiles: (A) 150 μm; (B) 300 μm; (C) 500 μm; (D) 700 μm; (E) 850 μm.

Deterring Process

The required quantities of propellant base grain, methylcentralite, and water are added to a rotating pan. Steam is injected directly into the rotating pan allowing the temperature to rise to 90–95°C and held at this temperature for 30 min. After coating is completed, the contents of the pan are placed in a hessian cloth bag and placed in a hot water steep (90–95°C) for 22 h. The powders are then air dried at 43°C.

Calibration Standards

A number of calibration standards were prepared of known weights of MC in NC and NC/NG matrices to obtain a calibration graph for quantitative determination of the concentration profiles, i.e., 2.5, 5.0, 7.75, 10.5, 16.9, and 24.4% *w*/w MC/NC and 4.75, 9.9, 14.5, and 20.6% *w*/w MC/(NC/NG).

Raman Microspectroscopy

A modified Nikon Optiphot metallurgical microscope optically coupled to a J-Y HG-2S double monochrometer was used in this study.[10] The faced-off grains were attached to a glass microscope slide with double-sided adhesive tape and Raman spectra were taken at 5-μm intervals from the outer edge inward and 5-μm intervals from the central perforation edge outward.

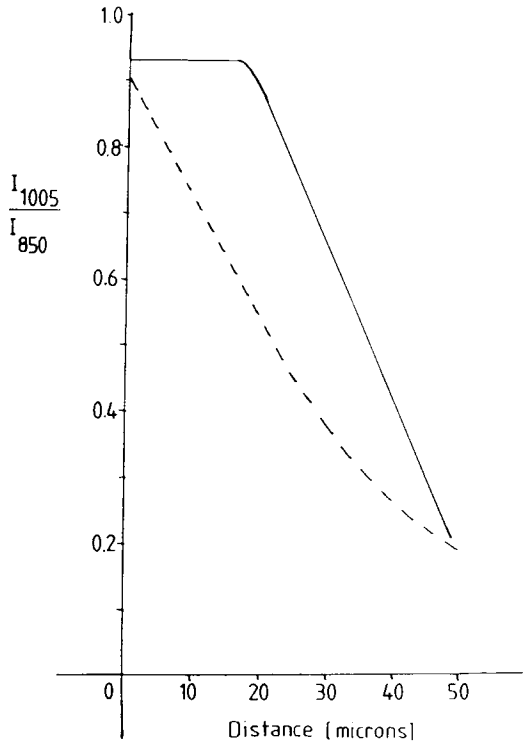


Fig. 7. Mean external and internal concentration profiles of longitudinal section: (——) external; (- - -) internal.

The laser and visible light paths are coincident so that the area that is visually selected is the area that is analyzed. The laser beam is focused to a diffraction limited spot size of 1 μm; thus it is possible to obtain Raman spectra at 1-μm intervals if required. A 100 $\times$ objective lens was used to view and collect the scattered Raman radiation using approximately 0.5 mW of 488 nm excitation, 1000 μm slit width, 50 cm^{-1}/min scan rate, 2 s time constant, and eight accumulated scans.

RESULTS AND DISCUSSION

The results of the work on methylcentralite/nitrocellulose propellant grains will be discussed first, and then the results on the methylcentralite/nitrocellulose/nitroglycerine.

Figure 1 shows the limited range Raman spectra (750–1050 cm^{-1}) of the calibration standards of the methyl centralite/nitrocellulose powders. The spectra are the sum of 10 individual spectra, each of which was obtained from

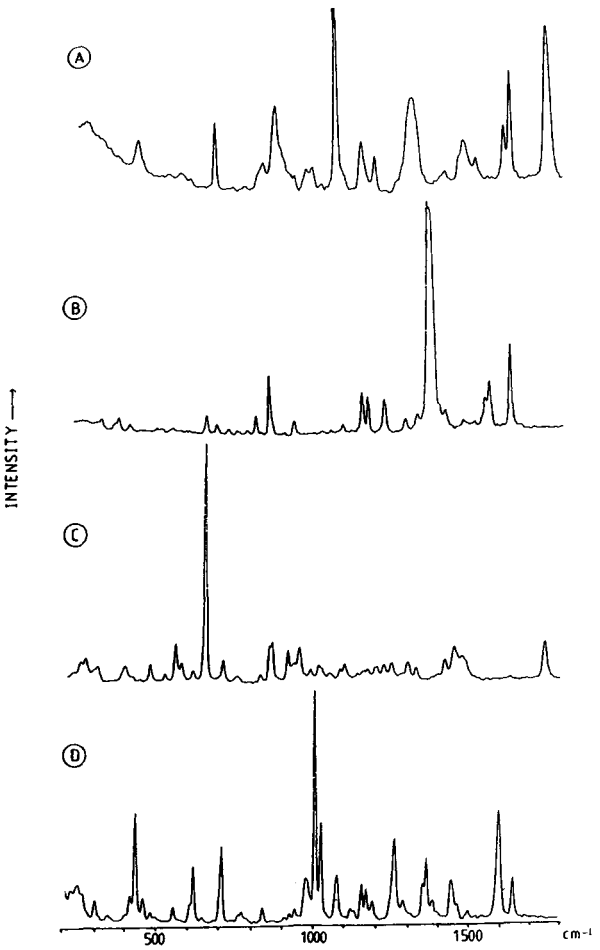


Fig. 8. Raman spectra of other deterrents: (a) di-*n*-butylphthalate; (b) dinitrotoluene; (c) camphor; (d) ethyl centralite.

a separate portion of powder. The peak at 850 cm^{-1} is assigned to the $-NO_2$ deformation of the nitrocellulose and the peak at 1005 cm^{-1} is assigned to the aromatic ring breathing vibration of the methylcentralite. The relative intensity at 1005 cm^{-1} with respect to 850 cm^{-1} (I_{1005}/I_{850}) vs. the methylcentralite (% by weight) gave a linear calibration plot shown in Figure 2.

A number of granules were chosen at random from the same batch and the concentration profiles obtained for the external and internal surfaces. The profiles for the external and internal surfaces are shown in Figures 3 and 4, respectively. In all cases for the external profile the same basic pattern is observed, a level concentration with a gradual cutoff point, though with some variation granule-to-granule in the concentration level and depth penetration being observed. The internal profiles show much greater variability; not only were the same granule to granule variations found as in the external surface but in two cases a different concentration profile was observed. Further investigation showed that this variation in profile was found in the two granules with the smallest perforation diameter (~ 180 μm), whereas the

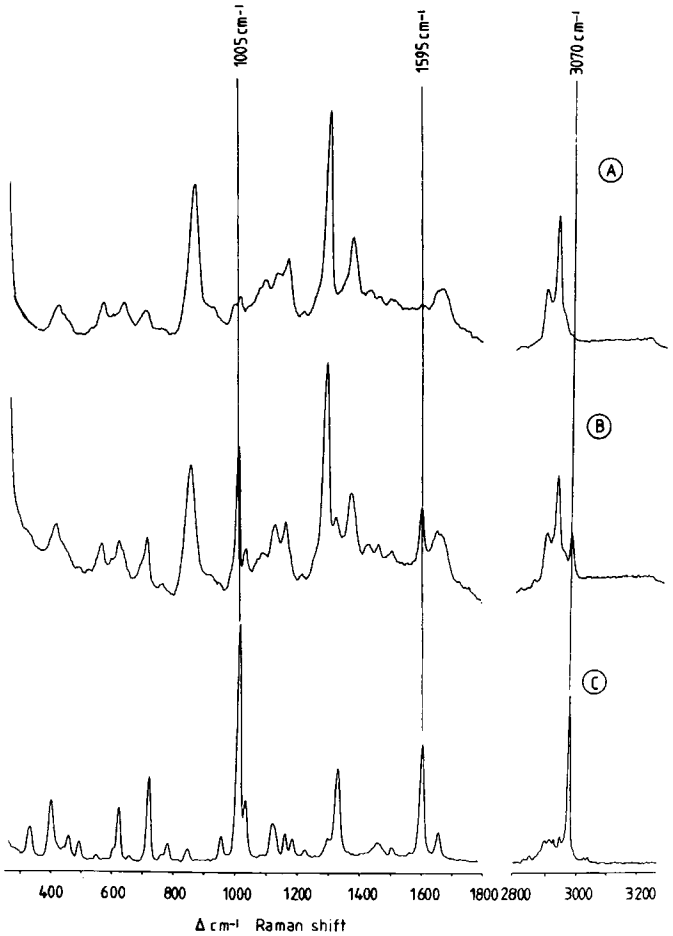


Fig. 9. Raman reference spectra of (a) nitrocellulose/nitroglycerine base grain, (b) NC/NG deterred with methyl/centralite, and (c) methyl centralite deterrent.

other granules had perforation diameters in the range (200–300 μm). These results indicate that the perforation diameter may have a significant effect on the concentration profile.

Although the nominal perforation size of the granules is 0.17 mm, great variability was found in the perforation size and shape in the granules examined. Quinlan[2] reported a similar variability in the perforation size, shape, and position.

In an effort to determine the variation within an individual granule, a granule was microtomed longitudinally and the Raman spectra were obtained at 150-μm steps along the length of the granule and at 5-μm steps from both the external and internal surfaces to a depth of 50-μm from each. The profiles are shown in Figures 5 and 6, respectively. The profile obtained for the external surfaces was found to be similar at all the positions studied whereas the internal profile exhibits the duality of profiles. Figure 7 shows the mean external and internal concentration profiles for the granule studied. These results indicate the variability of the concentration profiles from granule to granule and even some intragranular differences may occur.

In order to determine the utility of the technique to study the concentration profiles of different moderant systems, a number of materials have been investigated. These included ethyl centralite, camphor, dinitrotoluene, and dibutylphtalate. Their Raman spectra are shown in Figure 8. Initial results indicate that the Raman technique would be capable of detecting these materials within a nitrocellulose matrix.

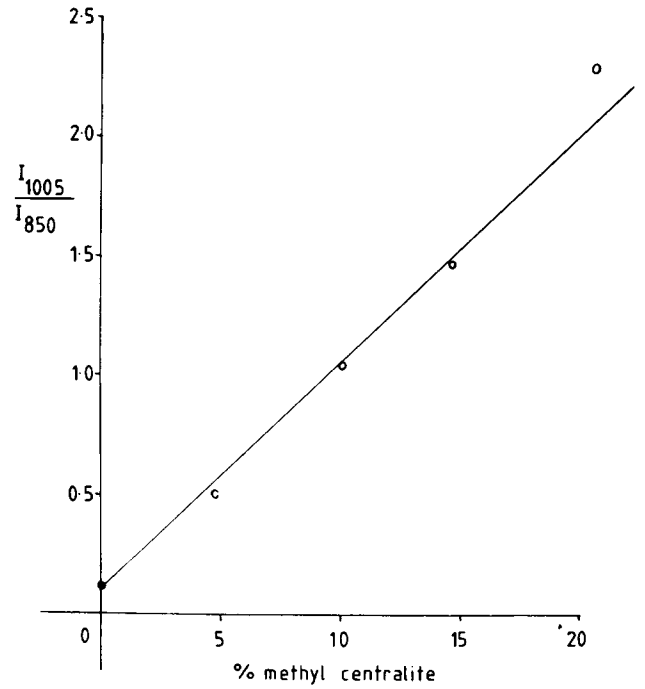


Fig. 10. Calibration graph of % w/w methyl centralite incorporated into NC/NG matrix vs. I_{1005}/I_{850}.

Reference spectra of NC/NG base grain, NC/NG deterred with methyl centralite (MC), and methyl centralite deterent are shown in Figure 9. Several bands due to the MC deterrent are clearly detected in the deterred NC/NG spectrum, e.g., the 1005 cm^{-1} aromatic ring breathing mode, the 1595 cm^{-1} aromatic ring stretch, and the 3070 cm^{-1} aromatic CH stretch. Therefore, intensity measurements of any of these unique vibrations relative to intensity measurements of the NC/NG vibrations (e.g., NO_2 deformation at 850 cm^{-1} or NO_2 symmetric stretch at 1290 cm^{-1}) can be used to determine the concentration profile. In this study the relative intensity ratio I_{1005} I_{850} was used to determine the concentration profile.

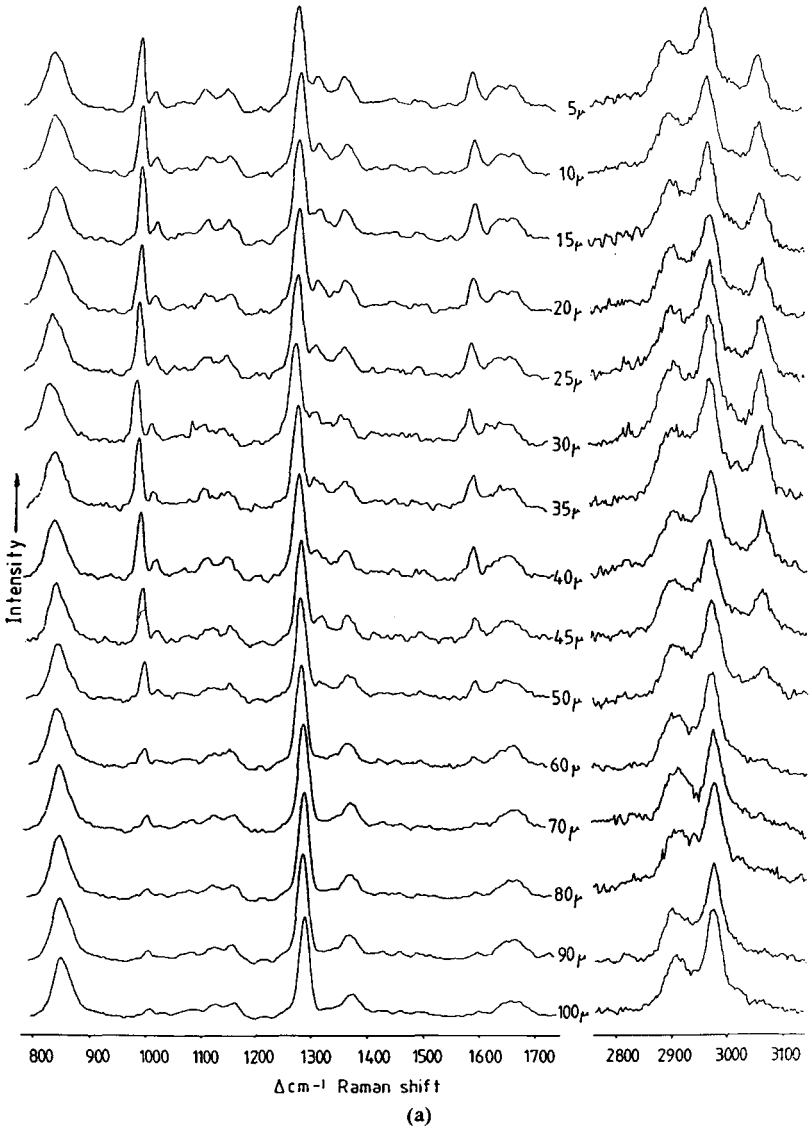
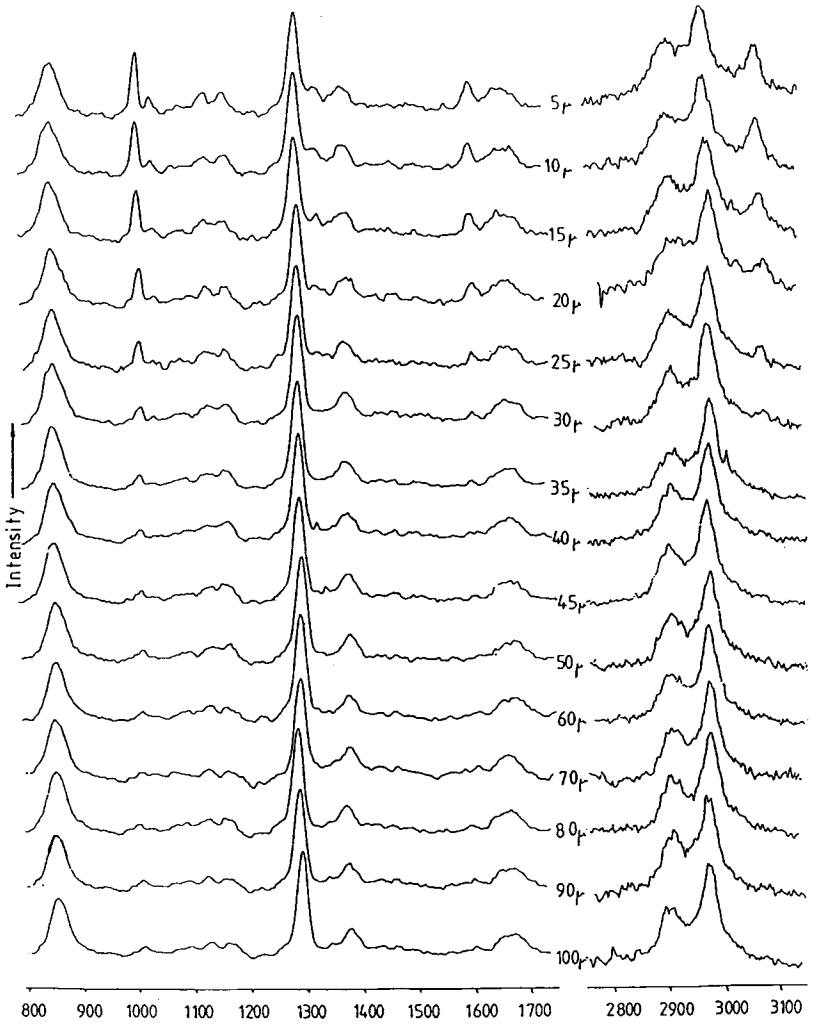


Fig. 11. Raman spectra of MC deterred NC/NG grain with perforation size < 200 μm: (a) distance from external edge; (b) distance from perforation edge.



(b)

Fig. 11. (*Continued from the previous page.*)

The calibration graph of relative intensity of I_{1005}/I_{850} vs. weight of MC is shown in Figure 10 showing a linear relationship. Figures 11(a) and 11(b) show the Raman spectra obtained at 5-μm intervals to 50 μm and then 10-μm intervals to 100 μm from the internal edge (external profile) and from the perforation edge (internal profile). These particular spectra were obtained from a grain with a perforation size of < 200 μm. The external spectra show the penetration depth of approximately 60 μm and the internal spectra show a penetration of 30 μm.

On examining the propellant grains through a stereomicroscope, the perforation size was observed to be nonuniform throughout the sample grains.

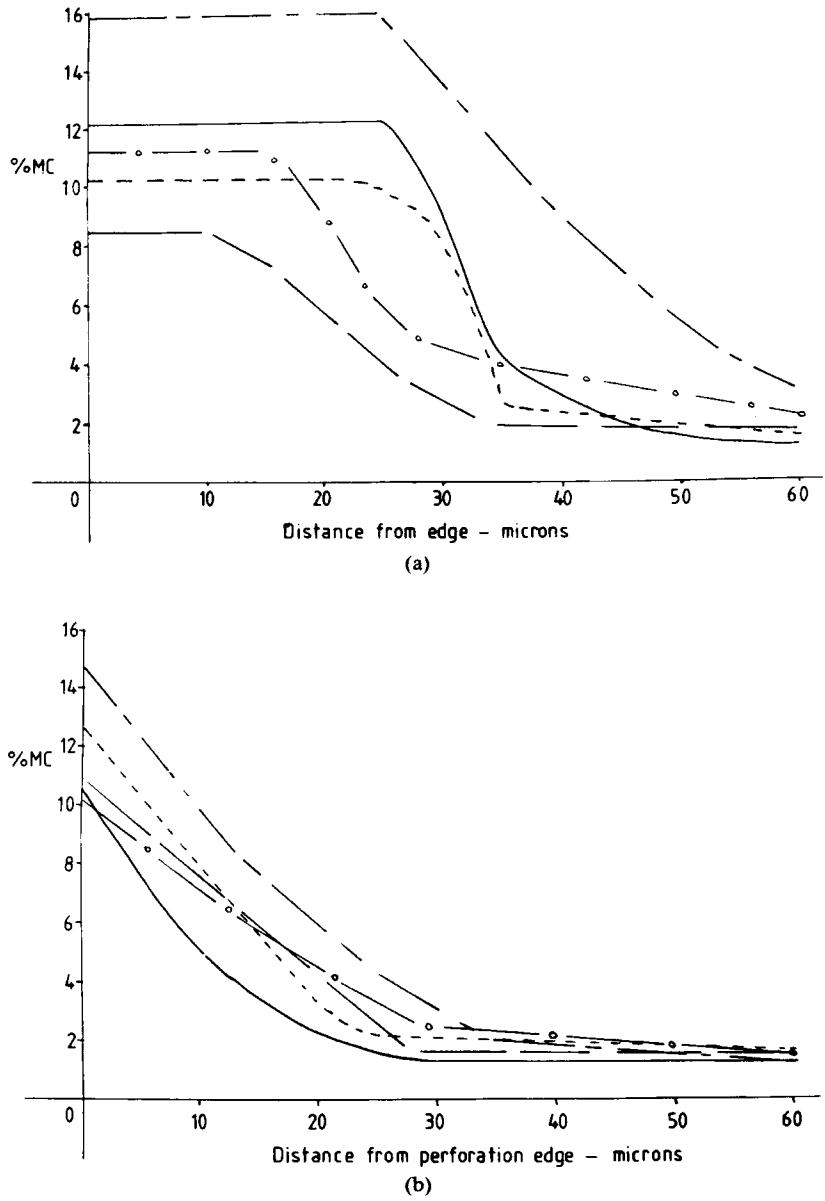


Fig. 12. Concentration profiles for MC Deterred NC/NG grains with perforation size < 200 μm: (a) external edge profile; (b) internal edge profile.

Therefore, two sets of grains from the same sample were examined by Raman microspectroscopy. One set had perforation size > 200 μm and the second set, perforation size < 200 μm. Thirteen grains of each set were examined and their external and internal profiles determined. The deterrent concentration profiles of five grains with perforation size < 200 μm are shown in Figures 12(a) and 12(b). The external profiles show a level concentration of deterrent at the edge with either a sudden drop in concentration (diffusion with interaction mechanism[11]) or a level concentration of deterrent at the edge with

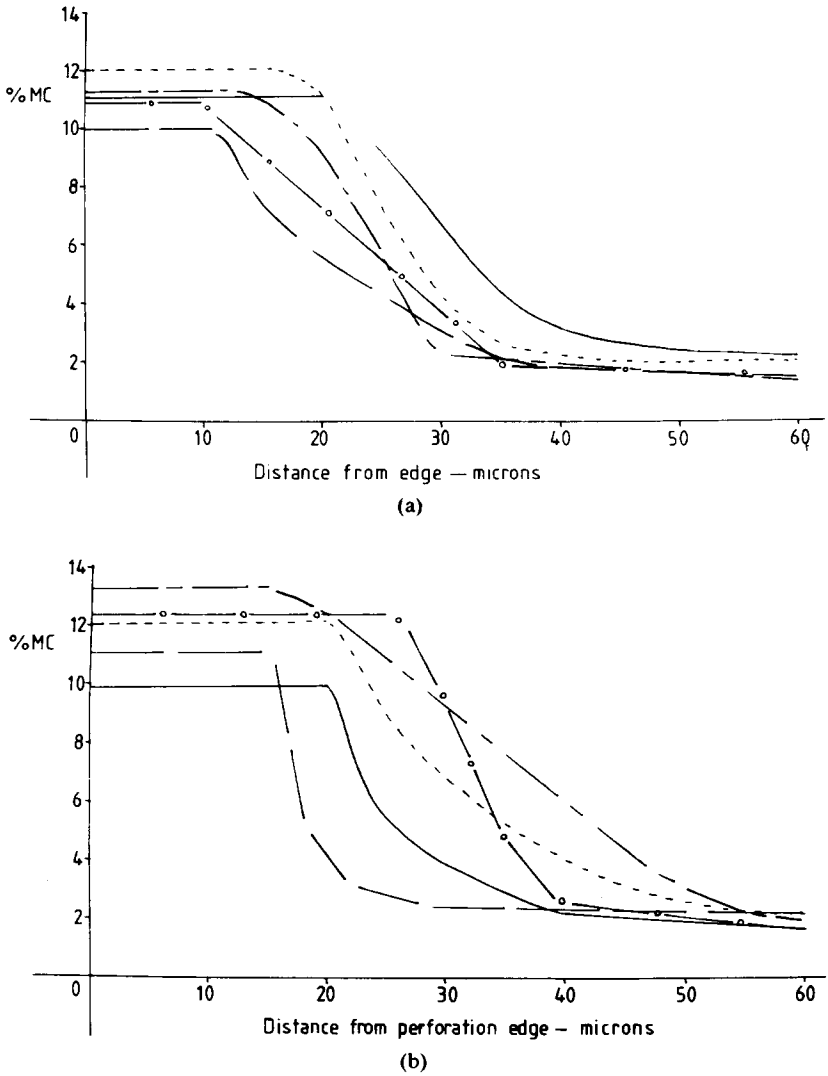


Fig. 13. Concentration for MC deterred NC/NG grains with perforation size > 200 μm: (a) external edge profile; (b) internal edge profile.

a more gradual decrease in concentration. The internal profiles all show a gradual decrease in concentration from the perforation edge inward.

The deterrent concentration profiles of five grains with perforation size > 200 μm are shown in Figures 13(a) and 13(b). Both the external and internal profiles exhibit the same shape, i.e., initial level concentration with either a sharp dropoff or gradual decrease in concentration. This data indicates that the perforation size has a marked effect on the internal concentration profile.

The deterrent profiles varied from grain to grain within the sample, showing differences in the concentration level and penetration depth. These variations are not unexpected due to the deterring method used.

CONCLUSIONS

Raman microspectroscopy is capable of providing qualitative and quantitative data on the concentration and penetration profiles of methyl centralite deterrent in a double-base nitrocellulose/nitroglycerine matrix and single-base nitrocellulose matrix.

The external profiles are consistent with Brodman et al.'s[5,11-13] diffusion with interaction mechanisms, i.e., a high concentration of deterrent molecules that are bound tightly through hydrogen bonding between carbonyl groups of the deterrent and the unesterified hydroxyl groups in nitrocellulose/nitroglycerine. The internal profiles have been shown to be dependent on perforation size in the extruded matrix.

Initial examination of different moderants indicate the possibility of obtaining concentration profiles on other moderant/nitrocellulose systems by the Raman technique. The advantage of the Raman technique is the high spatial resolutions obtainable (1 μm) compared with the 1R method (25–50 μm).

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References

1. J. B. Quinlan, "A Microscopic Examination of Extruded Double-Base Propellant," Frankford Arsenal Report R-1302, Dec. 1955.

2. J. B. Quinlan, *Microscope*, **14**, 385 (1965).

3. M. E. Levy, "Microscopic Studies of Ball Propellant," Frankford Arsenal Report R1286, Sep. 1955.

4. A. H. Milford, Winchester-Weston Division Technical Report No. WWR-68-2, Jan.–Dec. 1967.

5. B. W. Brodman, M. P. Devine, R. W. Finch and M. S. MacClaren, *J. Appl. Polym. Sci.*, **18**, 3739 (1974).

6. Olin Corporation Final Progress Report for Period Aug. 31–Nov. 30 1970, contract DAAA-25-70-C-0140.

7. H. Meier, D. Boesche, G. Zeither, E. Zimmerhackl, and W. Hecker, Bundesministerium de Verteidigung, Report BMVg-FBWT-79-14, Bonn, Germany, 1979.

8. J. D. Louden, J. Kelly, and J. Phillipson, *J. Raman Spectrosc.*, **18**, 137 (1987).

9. E. Varriano-Marston, *J. Appl. Polym. Sci.*, **33**, 107 (1987).

10. B. W. Cook and J. D. Louden, *J. Raman Spectrosc.*, **8**, 249 (1979).

11. B. W. Brodman, M. P. Devine, and M. T. Gurbarg, *J. Appl. Sci.*, **18**, 943 (1974).

12. B. W. Brodman, M. P. Devine, and M. T. Gurbarg, *J. Macromol. Sci. Chem.*, **A8**, 837 (1974).

13. B. W. Brodman, J. A. Sipia, Jr., and S. Schwartz, *J. Appl. Polym. Sci.*, **19**, 1905 (1975).

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