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## The Distribution of Natural Stable Isotopes of Carbon As a Possible Tool for the Differentiation of Samples of TNT

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Differentiating between samples of explosives of the same chemical nature by chemical or physical techniques is as yet one of the unsolved problems of forensic science. The techniques utilized, such as identification of impurities by gas chromatography [1], thin-layer chromatography [2], and nuclear magnetic resonance (NMR) spectroscopy [3], were primarily employed for quality control purposes and have not so far provided an acceptable method for either identifying the manufacturer of the explosives or differentiating or correlating between samples of explosives. The failure of those techniques for this particular purpose is primarily due to partial degradation of the explosives during storage. Therefore, the original pattern of impurities may completely change with time. The present report describes a novel, and potentially useful, technique for differentiating or correlating samples of 2,4,6-trinitrotoluene (TNT), which is hardly affected by the postmanufacturing history of the explosives.

Measurement of the variation in  $^{13}\text{C}/^{12}\text{C}$  ratios in natural materials is one of the most powerful techniques in elucidating the geochemistry of carbon. Several reviews have been written on this subject, such as those by Epstein [4] and Degens [5]. The fact pertinent to the present report is the ability of plants to discriminate between  $^{13}\text{C}$  and  $^{12}\text{C}$  during photosynthetic fixation of atmospheric  $\text{CO}_2$ . The degree of fractionation differs between continental plants and subaquatic plants which utilize dissolved  $\text{CO}_2$ , which has different isotopic composition from that of atmospheric  $\text{CO}_2$ . Additional fractionation occurs during the diagenesis of plant organic matter into coal or petroleum. Therefore, any petrochemical is expected to have  $^{13}\text{C}/^{12}\text{C}$  ratios depending on the isotopic composition of its parent material.

Another possibility of discriminating between isotopes is the rearrangements occurring during the cracking of petroleum and coal. The isotopic composition of each cracked fraction would depend on the initial isotopic composition of the crude oil and on possible complete or partial isotopic exchange during the manufacturing process.

The rationale behind the present study was to check whether the processes enumerated above may cause a distinct "fingerprint" for batches of TNT samples. The expected variation would be due to the use of different source materials and the difference in manufacturing processes in various plants.

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### Materials and Methods

Samples of TNT of known country of origin (but unknown date of manufacturing) were obtained from the central laboratories of the Israeli Police through the courtesy of Mr. S. Zitrin. The samples will be referred to following the country of manufacture, although it is not known as yet how representative they are. The use of country designation is for convenience only.

The experimental procedures are treated in a fairly detailed way. This is because of the general lack of familiarity of most chemists with the procedures employed in analysis for natural abundance of stable isotopes.

The samples of the explosives were converted to purified CO<sub>2</sub> gas for mass spectrometric measurements. The procedure for combustion was as follows. A 5-mg sample was weighed into a porcelain boat, which was precombusted to remove possible carbonaceous contaminants. The boat was introduced into a quartz combustion tube which fitted in a Fisher microcombustion resistance furnace. The combustion tube included a 6-cm plug of microanalytical CuO or Cuprox® (platinum-copper oxide catalyst manufactured by Coleman, Inc.). One end of the combustion tube was closed by a clamped spherical joint, through which the boat could be introduced. The other end of the tube was connected to a high vacuum system. The combustion tube had a side arm for the introduction of oxygen. During the analysis, oxygen was flowing through the system at subatmospheric pressure (around 400 mm Hg). For the combustion, the tube was flushed with oxygen and the furnace was heated to about 950°C. The boat was pushed into the furnace zone by moving an external magnet, which in turn pushed a quartz-enclosed bar magnet which was just behind the combustion boat. The combustion was continued for about 4 min. The oxygen was then shut off and the residual oxygen was pumped away. The evolved CO<sub>2</sub> was purified as far as possible by distillation (on the vacuum line) between dry ice-acetone and liquid nitrogen traps. Due to the high nitrogen content (20% by weight) of the TNT, the CO<sub>2</sub> samples always contained some nitrogen oxides, as indicated by the brown color of the evolved gas. Since nitrogen oxides can cause severe interferences in measurements of <sup>13</sup>C/<sup>12</sup>C ratios in CO<sub>2</sub> (N<sub>2</sub>O, for example, cannot be resolved from CO<sub>2</sub> under the experimental conditions utilized), the CO<sub>2</sub> was purified by circulating it with an automatic Toepler pump for 10 min over a Cu-containing furnace at 450°C. The nitrogen oxides were converted to elemental nitrogen gas which was separated from the CO<sub>2</sub> by freezing the latter in liquid air and pumping the nitrogen away.

The <sup>13</sup>C/<sup>12</sup>C measurements were made on an M-86 Varian-Mat® double inlet-double collector isotope ratio mass spectrometer. The results are expressed in the δ notation according to the formula:

$$\delta^{13}\text{C}(\text{‰}) = \left( \frac{{}^{13}\text{C}/{}^{12}\text{C}_{\text{sample}}}{{}^{13}\text{C}/{}^{12}\text{C}_{\text{standard}}} - 1 \right) \times 1000$$

The data are reported against the Chicago-PDB carbonate standard. Although the precision in our laboratory for <sup>13</sup>C/<sup>12</sup>C measurements is usually about ±0.25‰, we found the reproducibility of the TNT samples to be somewhat poorer. We tentatively assign this scatter to incomplete removal of interfering gases. As all samples were run in replicates, the precision is given for each sample separately (Table 1).

TABLE 1— $\delta^{13}\text{C}$  values of samples of TNT from various countries (results versus PDB standard).

Country of Origin	Number of Replicate Analyses	Mean $\delta^{13}\text{C}$ , ‰	Standard Deviation
Britain (manuf. by ICI)	5	-25.10	0.29
U.S. (manuf. by Du Pont)	14	-28.64	0.19
Israel	6	-24.53	0.64
Italy	14	-30.00	0.42
Yugoslavia	11	-28.48	0.45
Hungary	11	-30.93	0.51
Canada	11	-29.75	0.64

### Results and Discussion

The  $^{13}\text{C}$  values of replicate samples are given in Table 1 and illustrated in Fig. 1. The range in  $\delta^{13}\text{C}$  values is close to 6‰, with the Israeli samples being more enriched in  $^{13}\text{C}$  and the Hungarian samples more depleted in  $^{13}\text{C}$  than the rest of the samples. The results indicate that it is possible to differentiate between samples of TNT using  $^{13}\text{C}$  values. The reasons for this variance are not known. According to Cier [6], all toluene is manufactured from coal or petroleum sources. Thus part of the variance may be due to difference in the initial isotopic composition of the parent material. Figure 1 illustrates the fact that usually petroleum derived from marine strata is more enriched in  $^{13}\text{C}$  than petroleum from continental strata. However, as marine-derived petroleum is much more common than continentally derived petroleum, and because marine petroleum is

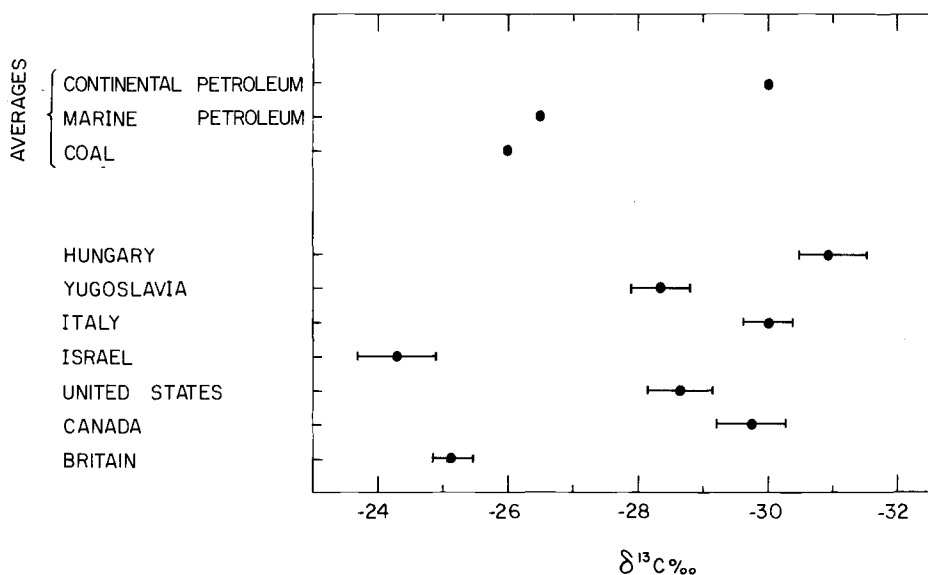


FIG. 1— $\delta^{13}\text{C}$  values of TNT samples from various sources compared with average  $\delta^{13}\text{C}$  values of coal and crude petroleum. (The horizontal bar represents the spread of  $\delta^{13}\text{C}$  values.)

isotopically close to coal, I tend to believe that the observed differences are introduced in the toluene manufacturing process. As the hydroforming process produces mixtures of aromatics and paraffins which will differ in their  $\delta^{13}\text{C}$  values, the type of process, the kind of catalyst, and the difference in reaction temperatures may bring about the observed variances. It is rather unfortunate that no specific details on the manufacture of both the toluene and the TNT of each sample could be obtained. Such data, in addition to actually measuring the initial and final products of the process, should be obtained in order to verify this hypothesis. However, the present results indicate that even without knowing the exact reason for the variance in  $\delta^{13}\text{C}$  values, those values are of diagnostic utility in differentiating samples of TNT. It is not known at present if this technique could be used in identifying more precisely the country of origin of the TNT. Conceivably the isotopic technique could be used for such a purpose, because the sources of toluene and the commercial practices in making TNT would probably not change markedly within a relatively short time. However, in order to establish this, much more would have to be known about the variation with time in the products of a single country or a single manufacturer.

### Conclusion

The present report describes the natural variations of the  $^{13}\text{C}/^{12}\text{C}$  ratios in TNT from different sources. The power of this technique at its present stage to discriminate between various samples is somewhat limited and more samples must be analyzed before it can be accepted as a generally reliable method. However, even at its present stage its power is not necessarily in identifying the source of each sample of TNT, but in the possibility of correlating or discriminating between samples. The inherent strength in using the natural distribution of isotopes is that, as long as the source of the chemicals used to prepare the explosives is the same, partial degradation would not alter the results. Moreover, the present report describes the use of isotopes of a single element, carbon. It is quite possible that by using a three-coordinate system of carbon, hydrogen, and nitrogen natural isotope distribution, a much less ambiguous identification of each sample can be established.

### Summary

TNT samples from different countries are shown to have different  $^{13}\text{C}/^{12}\text{C}$  ratios. The  $\delta^{13}\text{C}$  spread (against the PDB standard) is about 6.5‰.  $^{13}\text{C}/^{12}\text{C}$  ratios can therefore be utilized in order to correlate or discriminate between samples of TNT.

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### References

- [1] Gehring, D. G. and Shirk, J. E., "Separation and Determination of Trinitrotoluene Isomers by Gas Chromatography," *Analytical Chemistry*, Vol. 39, No. 11, 1967, pp. 1315-1318.
- [2] Yasuda, S. K., "Identification of Impurities in  $\alpha$ -Trinitrotoluene by Thin Layer Chromatography," *Journal of Chromatography*, Vol. 13, 1964, pp. 78-82.

- [3] Gehring, D. G. and Reddy, G. S., "Nuclear Magnetic Resonance Examination and Determination of the Di- and Trinitrotoluene Isomers in 2,4,6 Trinitrotoluene," *Analytical Chemistry*, Vol. 40, No. 4, 1968, pp. 792-795.
- [4] Epstein, S., *Distribution of Carbon Isotopes and Their Biochemical and Physiological Aspects*, R. E. Forster, I. T. Edsall, A. B. Otis, and F. J. Roughton, Eds., National Aeronautics and Space Administration, Washington, D.C., 1969.
- [5] Dogens, E., "Biogeochemistry of Stable Carbon Isotopes" in *Organic Geochemistry*, G. Eglinton and M. T. J. Murphy, Eds., Springer-Verlag, Berlin and New York, 1969, pp. 304-329.
- [6] Cier, H. E., "Toluene" in *Encyclopedia of Chemical Technology*, 2nd ed., Mrak, J. J. McKetta, and D. F. Othmer, Eds., Wiley Interscience, New York, Vol. 20, pp. 527-565.

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