

Note

Modification to a thermal energy analyzer with associated electronic filtering for improved gas chromatographic analysis of explosives traces

D. A. COLLINS

Home Office Forensic Science Laboratory, Priory House, Gooch Street North, Birmingham B5 6QQ (U.K.)

(First received May 10th, 1989; revised manuscript received August 29th, 1989)

Capillary gas chromatography (GC) in conjunction with the thermal energy analyzer (TEA) has found use in the analysis of explosives residues in and below the nanogram range^{1,2}. Initial use of the technique in this laboratory was disappointing in that poor peak shapes, more akin to packed-column peaks, were obtained. This was in agreement with the observations of Douse³, who subsequently recognised this phenomenon as electronic in origin. He circumvented the problem by connecting the TEA's photomultiplier to an external amplification and filtration system⁴.

This paper identifies the source of the peak broadening within the electronic circuitry of the TEA and describes a very simple modification—the replacement of a single capacitor—which results in very much better capillary GC peak shapes. A supplementary electronic filter to reduce noise is also described.

EXPERIMENTAL

A mixture of explosives and related compounds (identified in the caption to Fig. 2) was prepared in analytical-reagent grade ethyl acetate. This was injected into the GC-TEA system to obtain the chromatograms reproduced in this paper.

Gas chromatography

The gas chromatograph was a Carlo Erba 2900 series fitted with a water-cooled on-column injector. Originally a BPI capillary column was used, later replaced with a bonded-phase SE-52/-54 type. Apart from a lower temperature programming rate of 16°C min⁻¹ the GC conditions were not materially different from those used by Douse⁴.

Thermal energy analyzer

The TEA was a Thermo Electron Model 610. Interface and pyrolysis temperatures of 250° and 850°C, respectively, were employed.

Modification of the TEA

Inspection of the circuit diagram⁵ for the TEA's amplifier revealed a resistor and capacitor (R6 and C2) network around the first integrated circuit amplifier (A1)

having a time constant (product of resistance and capacitance) of about 2.3 s. This appeared to be the dominant factor in determining the response time of the whole instrument. The original capacitor C2 ($0.47\ \mu\text{F}$) was first replaced with a $0.1\text{-}\mu\text{F}$ component and later with a $0.022\text{-}\mu\text{F}$ capacitor. Metallised polyester capacitors of 10% tolerance and 250 V d.c. rating were used.

Electronic filter

A supplementary electronic filter for use in conjunction with the modified TEA was constructed; its circuit is shown in Fig. 1. The first stage around IC1 is a standard non-inverting amplifier with a voltage gain of about 100. The second stage around IC2 is a low-pass filter based on the well-known arrangement of Sallen and Key (see ref. 6) with a voltage gain of 1.6 to achieve the optimal Butterworth response. Two banks of capacitors with switched selection for nominal time constants of 0.1, 0.2, 0.5, 1, 2 and 5 s were provided.

The filter was constructed from standard electronic components from various sources. The 741 operational amplifiers were 8-pin d.i.l. (dual in line) plastics encapsulated. The resistors were 0.6 W 1% tolerance metal film types. (These were conveniently to hand; it is not suggested that very close tolerance components are essential.) The capacitors were metallised polyester, variously of 10% or 20% tolerance with 100 V d.c. rating. The higher capacitances used here are commonly available in the form of electrolytic capacitors. The latter type were avoided because of the leakage currents associated with them and because of the inability of the proposed circuit to provide the well-defined polarising voltages which they normally require. The filter unit was originally powered with $\pm 9\ \text{V}$ supplies obtained from a pair of 9 V dry batteries. Subsequently it was found that it could very conveniently be powered directly from the TEA with $\pm 15\ \text{V}$ supplies. These were taken from points Z and Y on the edge connector into which the TEA's amplifier circuit board locates. The current consumption of the prototype filter at $\pm 15\ \text{V}$ was only 1.5 mA.

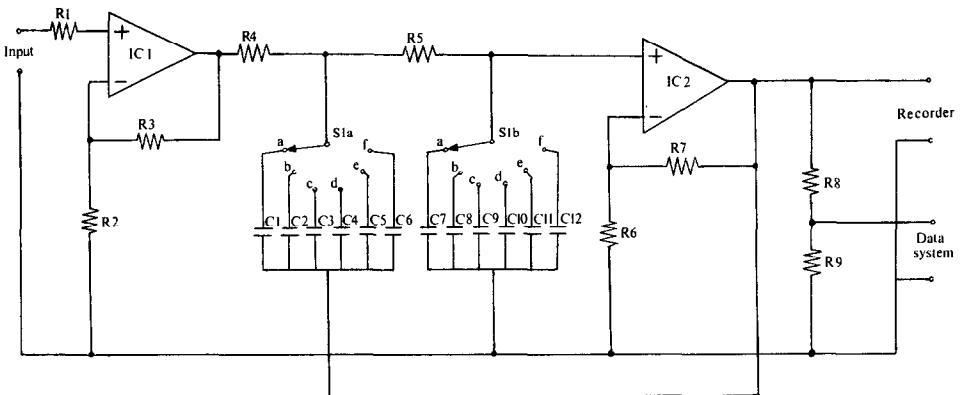


Fig. 1. Circuit of electronic filter unit. IC1, IC2 = 741 type integrated circuit operational amplifiers; R1, R2 = $10\text{-k}\Omega$, R3, R4, R5 = $1.0\text{-M}\Omega$, R6 = $5.6\text{-M}\Omega$, R7 = $3.3\text{-M}\Omega$, R8 = $150\text{-k}\Omega$ and R9 = $1.0\text{-k}\Omega$ resistors; C1, C7 = $0.1\text{-}\mu\text{F}$, C2, C8 = $0.22\ \mu\text{F}$, C3, C9 = $0.47\text{-}\mu\text{F}$, C4, C10 = $1.0\text{-}\mu\text{F}$, C5, C11 = $2.2\text{-}\mu\text{F}$ and C6, C12 = $4.7\text{-}\mu\text{F}$ capacitors; S1a, S1b = ganged 2-pole-6-way switch to give selected time constants of nominally: a = 0.1, b = 0.2, c = 0.5, d = 1, e = 2 and f = 5 s.

The input to the filter was taken from the 10 mV recorder output on the TEA. The direct output from IC2 was monitored at 2 V span on a conventional pen recorder. The pair of resistors R8 and R9 formed a potential divider which permitted the filter to be matched to the 10 mV sensitivity of the Trivector Trilab data system on which the chromatograms shown here were recorded.

RESULTS AND DISCUSSION

Fig. 2 shows a chromatogram of the mixture of explosives and related compounds (approximately 1 ng of each) using the TEA without supplementary filtering and with the original C2 (0.47 μ F) in place. Fig. 3 shows the same mixture similarly chromatographed after C2 was replaced with the 0.1 μ F component. The substitution of the lower value capacitor resulted in appreciably improved peak shapes. Unfortunately, more noise was evident, an effect similar to that observed by Douse with his arrangement.

The noise became obtrusive at higher sensitivities. Fig. 4 shows a similar mixture to that injected previously but at the level of approximately 100 pg per component. In this example C2 in the TEA had now been changed to 0.022 μ F, giving in

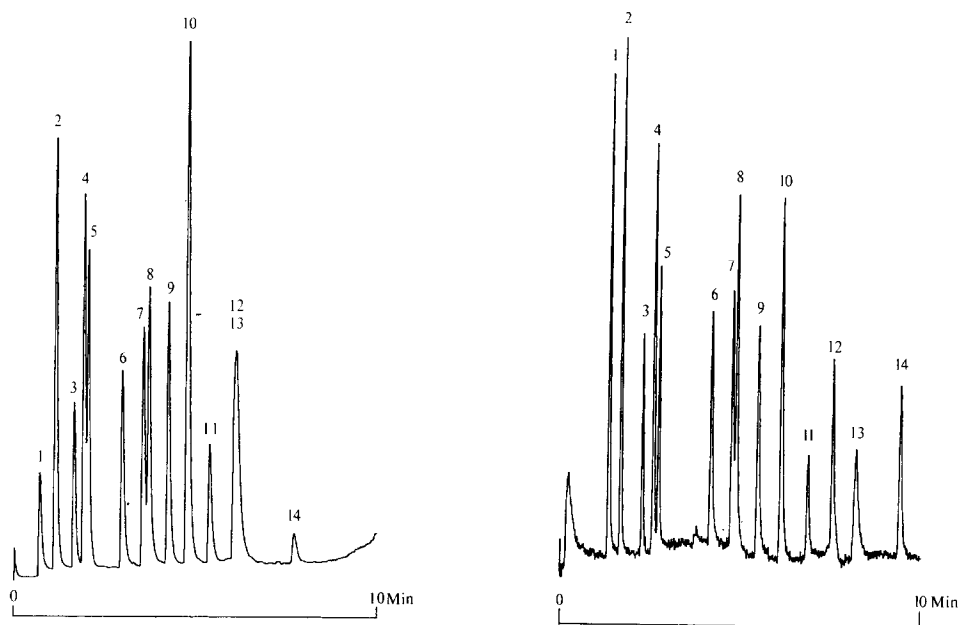


Fig. 2. Capillary (BPI) chromatogram of a mixture of explosives and related compounds (approximately 1 ng of each component) obtained directly from the unmodified TEA. Peaks: 1 = ethyleneglycol dinitrate (EGDN); 2 = nitrobenzene; 3 = 2-nitrotoluene; 4 = 3-nitrotoluene; 5 = 4-nitrotoluene; 6 = nitroglycerin (NG); 7 = 1,3-dinitrobenzene; 8 = 2,6-dinitrotoluene; 9 = 2,4-dinitrotoluene; 10 = isosorbide dinitrate; 11 = 2,4,6-trinitrotoluene (TNT); 12 = pentaerythritol tetranitrate (PETN); 13 = hexogen (RDX); 14 = tetryl.

Fig. 3. Capillary (SE-52/-54 type) chromatogram of a similar mixture to that in Fig. 1, obtained directly from the TEA after C2 was replaced with a 0.1- μ F capacitor.

combination with R6 in the TEA a time constant of about 0.1 s. No supplementary filtering was used. The very fast response time had negligible influence on the capillary GC peak shapes but it resulted in the unsatisfactory level of noise shown.

Fig. 5 shows a repeat injection of that made in Fig. 4, but obtained via the filter circuit described above, with a time constant of 0.5 s selected.

The improved noise level, while retaining an adequately sharp peak shape, is evident upon inspection.

No difference in performance of the filter circuit was observed using either dry batteries or the TEA as its power source.

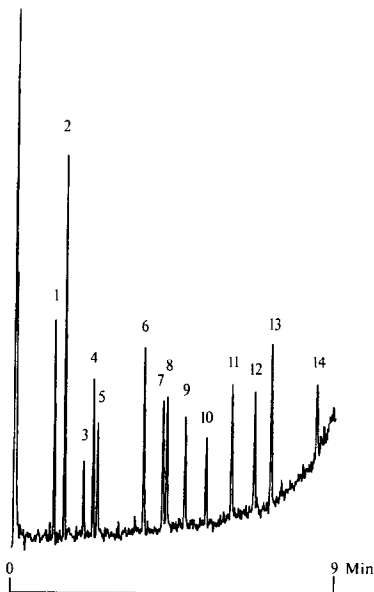
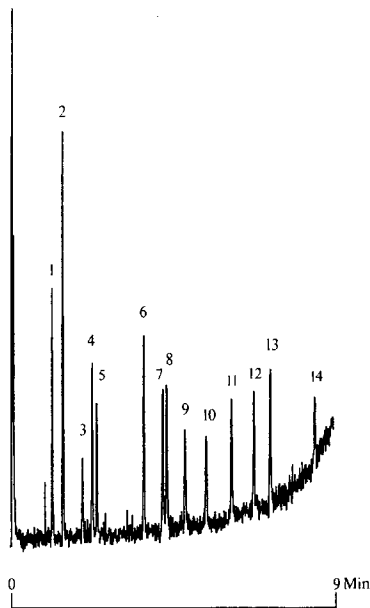


Fig. 4. Capillary (SE-52/-54 type) chromatograms of a mixture (approximately 100 pg each) of explosives and related compounds similar to that in Fig. 1 obtained directly from the TEA after C2 was replaced by a 0.022- μ F capacitor.

Fig. 5. Capillary (SE-52/-54 type) chromatograms of the same mixture as in Fig. 4, 100 pg per component, obtained from the TEA via the electronic filter unit, with a time constant of 0.5 s selected.

CONCLUSION

This paper has shown that with a very simple modification the TEA may be made fully compatible with the resolving power of modern capillary GC. With a capacitor of 0.022 μ F substituted for the original C2 in the TEA the performance of the whole system appears to be limited by the efficiency of the GC separation and the residual noise which seems to originate in the TEA's photomultiplier. At high sensitivities the noise can be minimised with suitable electronic filtration. Where such a filter provides a range of different time constants, the operator can make his own choice as to the compromise between the sharpness of the peaks and the level of noise he can tolerate. A filter circuit of the type described above could, of course, have other applications in chromatography or spectroscopy where noise is troublesome.

ACKNOWLEDGEMENT

I am grateful to J. M. F. Douse for furnishing me with additional information on his arrangement described in ref. 4.

REFERENCES

- 1 E. V. Goff, W. C. Yu and D. H. Fine, *Proc. Symp. Anal. Detect. Explosives, Quantico, VA, 1983*, NTIS, Springfield, VA, 1983, p. 159.
- 2 D. H. Fine, W. C. Yu and E. V. Goff, *Proc. Symp. Anal. Detect. Explosives, Quantico, VA, 1983*, NTIS, Springfield, VA, 1983, p. 169.
- 3 J. M. Douse, *J. Chromatogr.*, 328 (1985) 155.
- 4 J. M. Douse, *J. Chromatogr.*, 410 (1987) 181.
- 5 *Schematics for 543/610 Service Manual*, Thermo Electron Ltd., Waltham, MA.
- 6 M. H. Jones, *A Practical Introduction to Electronic Circuits*, Cambridge University Press, Cambridge, 1977.