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**Analysis Of Trapped Gas In 1E34
Detonators By Gas Chromatography**

**David K. Warner, Paul S. Back and
Brady V. Barnhart**

May 14, 1980

MOUND FACILITY

Miamisburg, Ohio 45342

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MONSANTO RESEARCH CORPORATION
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U. S. DEPARTMENT OF ENERGY

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Abstract

A method was developed to extract and then analyze gas trapped in thermally aged 1E34 detonators. This gas was extracted into an evacuated volume and injected into a gas chromatograph for separation and quantitative analysis. To effect this gas extraction, a device was designed for puncturing the detonator cup and capturing the effused gas. Limited testing of five detonators in this device shows amounts of gas ranging from about 0.5×10^{-7} to 12×10^{-7} moles.

Introduction

Several 1E34 detonators that were aged at 120°C for 11 to 12 months were shown by gauging measurements to have a "bulge-like" distortion of the top of the aluminum cup that encloses the explosive powder. As part of an effort to determine the cause of the distortion, this study was initiated to measure quantities of gas trapped within the detonators.* Specifically, our work included (1) the designing of a device used to puncture the detonator and collect the effused gas, (2) the integration of this device into the sampling system of a gas chromatograph (GC), and (3) the development of the sampling methodology.

Although this report focuses principally on the instrumentation and sampling methods, numerical results for five test units are presented that illustrate the quantities of gas involved, the breadth of the analysis, and the problems inherent in the procedures that have evolved.

*HMX powder has been reported to decompose to give the following product gases: CO, CO₂, N₂, N₂O, NO₂, NO, H₂O. See References.

Overview of instrumentation

A block diagram of the instrumental setup is shown in Figure 1. The helium carrier gas is finely regulated for flow rate, and it flows to the gas sampling valve. The gas sampling valve either directs the helium to the gas chromatograph while the sampling operations are proceeding in the gas collection device (path 1), or it directs the helium through the collection device to flush the sample to the gas chromatograph (path 2). The gas chromatograph then separates the sample into its components, and their detection and quantitative measurement complete the analysis sequence. More complete descriptions of several of these blocks follow.

Gas sampling valve

The gas sampling valve served as the focus of the sampling procedures, as it allowed the manipulation of the detonator gas collection device, the vacuum, and the gas manifold while isolating the chromatograph from these parts of the sampling system. The arrangement of tubing to the gas sampling valve is shown in Figure 2. Sketch A of Figure 2 shows the detonator gas collection device isolated from the flow of helium that is constantly required for the GC to function properly. In this

FIGURE 1. - Apparatus diagram for detonator gas experiments.

bypass arrangement, the detonator is punctured, and the released gas is collected for injection into the GC. A simple quarter turn of the sampling valve rotor gives the flow arrangement B (Figure 2) where the collected gas from the detonator is rapidly transferred to the gas chromatograph for analysis. Flow arrangements C and D (Figure 2) serve for calibration of the gas chromatograph. The gas sampling valve is a modified eight-port Valco model.

Detonator gas collection device

This device had to meet the following experimental requirements:

- (1) Capable of puncturing a detonator cup.

- (2) Small internal volume to effect a rapid and efficient transfer of sample gas to the GC.
- (3) Leak free to ensure the integrity of the sample, which most assuredly would contain air components.

The final design that was used in this work is shown as a cutaway representation in Figure 3, and a photograph of the device without the auxiliary helium supply pipe is shown in Figure 4.

Several comments about the device will aid in understanding its construction and functioning.

- (1) The puncturing shaft was constructed from the valve tip and shaft assembly of a Nupro SS-OKS-2

FIGURE 2 - Gas sampling valve flow arrangement.

FIGURE 3 - Detonator gas collection device.

FIGURE 4 - Photograph of gas collection device.

valve. A vertical notch was filed into the valve tip to provide a circular cutting action as the shaft handle is rotated and the tip descends. The hole cut in the detonator cup was approximately 1 mm in diameter. This cutting shaft threads into the body of the device and seats against an O-ring to provide leak tightness.

- (2) The cavity and pipe volume into which the gas escapes is approximately 1 ml in volume, small enough to be rapidly swept free of sample without significant exponential tailing in the cavity when the isolating valves are opened.
- (3) The detonator was held securely by the detonator support piece which is threaded into the bottom of the device body. The circular surface of the detonator cup rests against an O-ring, and the support

piece also compresses an O-ring for further leak tightness. In practice, the volume between the two O-rings was flushed with helium from the auxiliary supply before the support piece O-rings were finally seated. This helium supply was separate from the carrier gas that flows through the sample cavity, and helium pressure was maintained between the two O-rings throughout the experiment as an additional measure to prevent air from leaking into the sample cavity.

Gas chromatograph

This instrument is a Becker-Packard 419 with cryogenic cooling capability that allows the columns to be chilled with a liquid nitrogen supply. The 3 mm o.d. X 3-m column was packed with 80/100 mesh Poropak Q, and the helium carrier gas (99.9999% purity) flow was maintained at

30 ml/min. The column temperature was programmed to be held at -100°C for 5 min after sample injection, then linearly elevated at $20^{\circ}/\text{min}$ to a final temperature of 180°C where it is held for 9 min. The current through the rhenium-tungsten thermal conductivity detector filament was 150 mA, with a block temperature of 225°C . The chromatograph injection port was held at 110°C . The detector output was integrated with a Spectra Physics 4000 integrator.

Sampling procedure

- (1) The detonator was placed, cup side up, on the support piece which was then threaded into the device until the O-rings were touched; the support piece then was backed off $1/8$ turn, and a rapid helium flow was started through the auxiliary helium pipe. This flow was maintained for several minutes.
- (2) Simultaneously with #1, helium flowed through the cavity above the detonator. The purpose of these two steps was to flush air from the device before the detonator was seated against the O-rings.
- (3) After O-ring compression, the helium cover gas around the detonator body was increased to 20 psig, and the cavity above the detonator was evacuated to 100 μm or less, then refilled with helium. This evacuation and refilling was repeated three times or more. Finally, a vacuum of 100 μm or less was established in the cavity, and the isolation valves were closed.
- (4) The puncturing shaft was then threaded down into the detonator

and backed off, allowing gas within the detonator to expand into the evacuated cavity.

- (5) After the gas pressure in the detonator and cavity was allowed to equilibrate for 10 sec, the gas sampling valve was rotated, and isolation valves were immediately opened to flush the gas from the cavity into the GC column. The column temperature program was started at this time, and carrier gas flow through the gas collection device was maintained until the assay was completed.
- (6) A blank run (no puncture, but otherwise identical procedure) was performed prior to every actual detonator puncture run.

Experimental results and discussion

Since the number of parts (detonators) available for experimental work was limited, only five have been assayed by this procedure. A representative chromatogram is reproduced in Figure 5 illustrating the separation of the gaseous components of a sample, and a compilation of results for the five parts is shown in Table 1.

As in most investigations that deal with complex samples, these analytical results cannot be interpreted blindly without a review of the sample history. Results from this procedure may be used to infer the minimum amount of the observed gases present in the detonator when it was placed in the sampling device. These results cannot be used to resolve important

FIGURE 5 - Chromatogram of gases from part #287.

Table 1 - GASES DETECTED IN 1E34 PARTS

Component ^a	Part No.				
	L 001 SN 1446	L 001 SN 1352	L 001 SN 1362	L 002 SN 0256	L 002 SN 287
N ₂	0.188	9.093	0.208	0.149	6.333
O ₂	0.063	2.831	0.066	0.06 ^b	0.533
CO	0.394	0.065	0.04	0.073	0.641
NO	0.35	0.049	0.074	N.D. ^c	N.D. ^c
CO ₂	0.047	0.057	0.049	0.067	0.119
N ₂ O	0.091	0.168	0.118	0.214	0.333
Total	1.132	12.26	0.555	0.563	7.958

^aAll values X10⁷ moles.

^bEstimate.

^cN.D. - not detected.

peripheral questions about the historical characteristics of the detonation, such as:

- (1) Would high internal pressures, generated during thermal aging, be sufficient to breach the glue bond on the detonator, resulting in the release of decomposition gases and trapped air to the atmosphere?
- (2) Was the glue bond impermeable to air?

These questions are raised when one examines the results of Table 1, in particular the wide range of the air components, N_2 and O_2 . Since negative blank runs in our experiments rule out significant air leaks, one must seriously speculate about the peripheral questions raised above. In this sense, the results show the need for further investigation of the thermal aging process and the character of the glue bond if a complete answer to the cause and effect of internal gas pressure and cup distortions is forthcoming.

Conclusions

A system was devised for breaching 1E34 detonators and measuring the amount of effused gas that expands into an evacuated

cavity. The results are applicable to the part at the time of assay, but further investigations are necessary to confidently link these results to thermal aging test parameters. The analytical procedure separates and quantitatively measures six gas components at a detection limit of about 1×10^{-8} moles for each component. The experiments are amenable only to 1E34 detonators at the present time, but adaptations to other configurations is possible. Should a need be demonstrated for this type of analysis in the future, procedure improvements may be expected in the areas of trend prediction, error statements, and sensitivity limits. These are dependent upon having a larger data base from which to extract this information.

Acknowledgment

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References

1. C. U. Morgan and R. A. Beyer, Combustion and Flame, **36**, 99-101 (1979).
2. L. W. Collins and L. D. Haws, Thermochimica Acta, **21**, 1-38 (1977).

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