A Study of the Combustion Behaviour of Pyrotechnic Whistle Devices (Acoustic and Chemical Factors)

M. Podlesak* and M. A. Wilson**

*Weapons Systems Division, System Sciences Laboratory, DSTO, PO Box 1500, Edinburgh 5111, Australia

** Pains Wessex (Australia) Pty Ltd, PO Box 90, Lara 3212, Australia
Formerly of Weapons Systems Division, Aeronautical and Maritime Research Laboratory, DSTO, Melbourne, Australia

ABSTRACT

Pyrotechnic whistles have long been used in both civilian and military applications. It is known that, under certain conditions, these compositions burn in an oscillatory manner and have exhibited a tendency occasionally to explode with great power during combustion. Based on the results of experimental work and a study of the thermochemical properties of whistle fuels, a hypothesis is proposed that attempts to account for the observed high levels of explosive and acoustic power of pyrotechnic whistles. The formation of < 10 μm diameter hollow carbon spheres was observed in laboratory experiments involving the thermal decomposition of potassium benzoate (a whistle fuel) in a reducing atmosphere. At the moment of formation, the spheres may possibly be filled with combustible hydrocarbon gases and would be extremely reactive. If formed during the quiet cycles of an operating whistle device, their existence may explain the higher than expected acoustic power of pyrotechnic whistles. Such a hypothesis may also lead to an understanding of other hitherto unexplained explosions, where under conditions such as 'cook-off', the thermal decomposition of organic fuels used in some other pyrotechnics would result in the formation of new substances which are more reactive than the parent chemicals.

Keywords: whistle, combustion, acoustics, oscillating burning, pyrotechnics

1. Introduction

Pyrotechnic whistle compositions are usually formulations consisting of the salt of an aromatic acid such as potassium benzoate ($KC_7H_5O_2$) or sodium salicylate ($NaC_7H_5O_3$) as the fuel and a strong oxidant such as potassium perchlorate ($KClO_4$). When the powder mixture is consolidated and burnt as an open-faced pellet, it burns at a constant linear rate and emits virtually no sound. However, if the pressed composition is ignited at the bottom of a short tube, it burns in an oscillatory manner and emits a loud, high-pitch whistling sound.

Pyrotechnic whistles have been used in a number of military and civilian applications, however, it has long been known that whistles have a propensity to explode during combustion and have been responsible for serious injuries. As part of a study to reduce the hazards associated with the manufacture and use of whistles, an investigation was undertaken to determine the mechanism by which high intensity oscillatory sound is produced by the combustion of consolidated whistle formulations.

This is described in a more comprehensive report[1] where modern instrumentation techniques, including high speed video, were employed to examine the combustion characteristics of the whistle composition MRL(X) 418, which contains 30% potassium benzoate and 70% potassium perchlorate. In particular instances, comparisons were made between this composition and a US formulation, which incorporates sodium salicylate as the fuel.

In addition, it has been established through acoustic considerations that the energetic output of each cyclic pulse of a burning whistle device

is considerably greater than that expected from the thermochemical properties of the simple fuel-oxidiser system. Experimental evidence confirmed that when whistle composition was deliberately made to explode, sufficient energy was released to fragment the metal test cylinders into which it was filled. However, the projected fragments exhibited relatively large dimensions, with velocities not exceeding 100 m/s—factors indicating that detonation of the filling did not occur. When equal masses of other pyrotechnics, including flare composition and gunpowder (Black Powder) were similarly tested, no fragmentation of the cylinders was evident.[1]

These observations have led to the hypothesis that, under the specific conditions extant in the burning zone of a whistle device, highly reactive secondary fuels may be created through the thermal decomposition of the primary fuel. It is proposed that while these conditions occur during the quiescent phase of a burning whistle device, the resultant mass of reactants is limited by inherent physical control factors. However, should uncontrolled changes in the combustion surface geometry occur, the mass of these reactants can increase, leading to the explosion of the device.

2. Computer Modeling of Combustion

The NASA-Lewis CEC 76 computer code was used to predict the reaction products of a mixture of 70% $KClO_4$ and 30% $KC_7H_5O_2$ burning within a tube (i.e., in the absence of excess air). At atmospheric pressure, the predicted species consisted mainly of KCl, H_2O, CO_2 and CO; the latter two being in equal proportions. In an actual whistle device, it was questioned whether the subsequent reaction of hot CO in air at the tube mouth would generate sufficient acoustic energy to produce the oscillating sound inherent in this type of device.

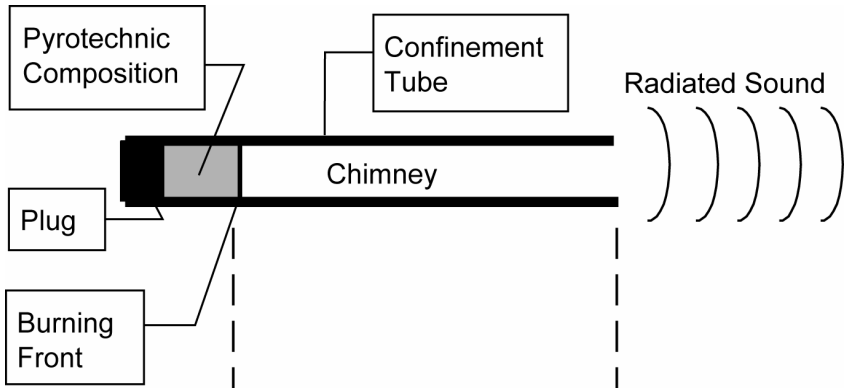
To test this contention, a pyrotechnic whistle was ignited inside an open drum from which the air had been displaced with argon. When compared with an identical whistle burning in an air-filled drum, no difference in either frequency or amplitude could be discerned, inferring that the oscillatory sound is produced within the tube, and most likely, at the burning front.

3. Acoustic Model

The acoustic model presented here is approximate and quite simplistic in as far as the following assumptions were used:

- the model is based on linear acoustic theory (the model is less accurate for large amplitude waves),
- the acoustic propagation properties of the gas in the chimney of the whistle are homogenous,
- the effect of gas flow on the acoustic wave propagation is neglected,
- the free field impedance of the acoustic propagation medium inside and outside the chimney is nearly the same, and
- thermal and viscous losses are neglected in the propagation of acoustic waves.

Figure 1 provides the basic framework for understanding the proposed acoustic model of the whistle device. The acoustic behaviour of the device has been modelled on the classic quarter-wave resonator, where the reaction front of the burning pyrotechnic composition provides both a high acoustic impedance boundary and an acoustic energy source, and the open end, or mouth of the whistle chimney, provides a low impedance boundary.



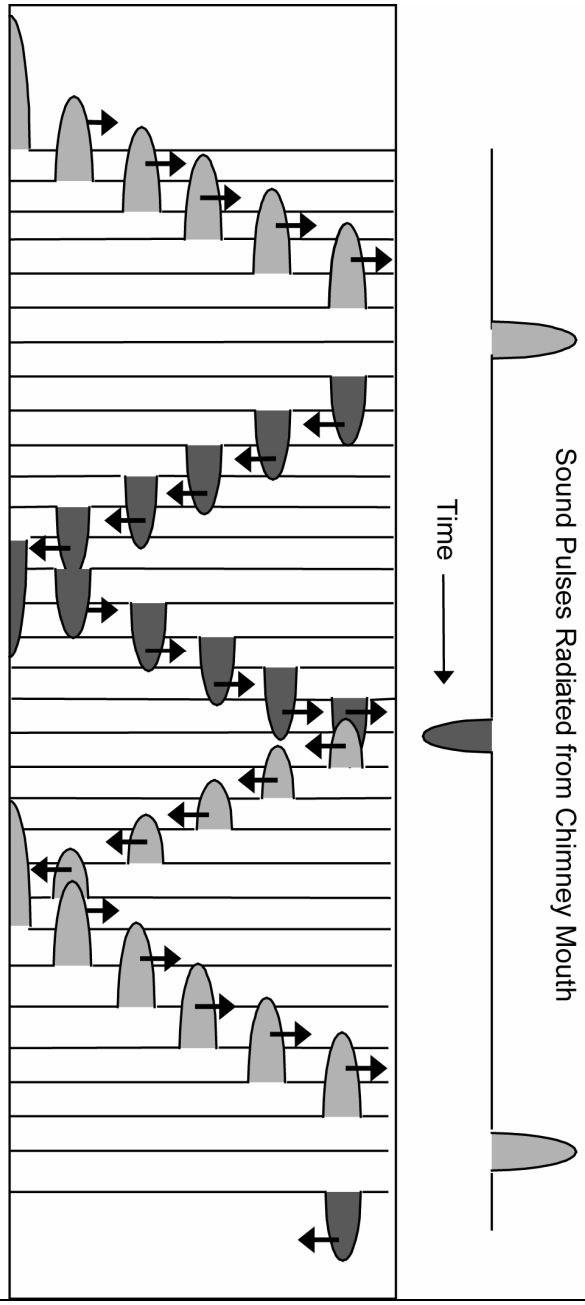


Figure 1. Schematic representation of a pyrotechnic whistle device showing an acoustic pressure pulse propagating through the chimney in a sequence of snapshots in time. Changes in pulse height occur at points of reflection. Positive pressure pulses have light shading whereas negative or rarefaction pulses have darker shading. The left-hand side of the time sequence box corresponds to the position at the burning front and the right-hand side to the position at the chimney mouth. Arrows indicate the direction of pulse propagation. A graph of radiated pressure pulses is shown on the right-hand side of the time sequence box. The radiated pressure pulses are generated each time the internal pressure pulse is reflected at the chimney mouth. A drop in the internal pulse height indicates this radiation loss.

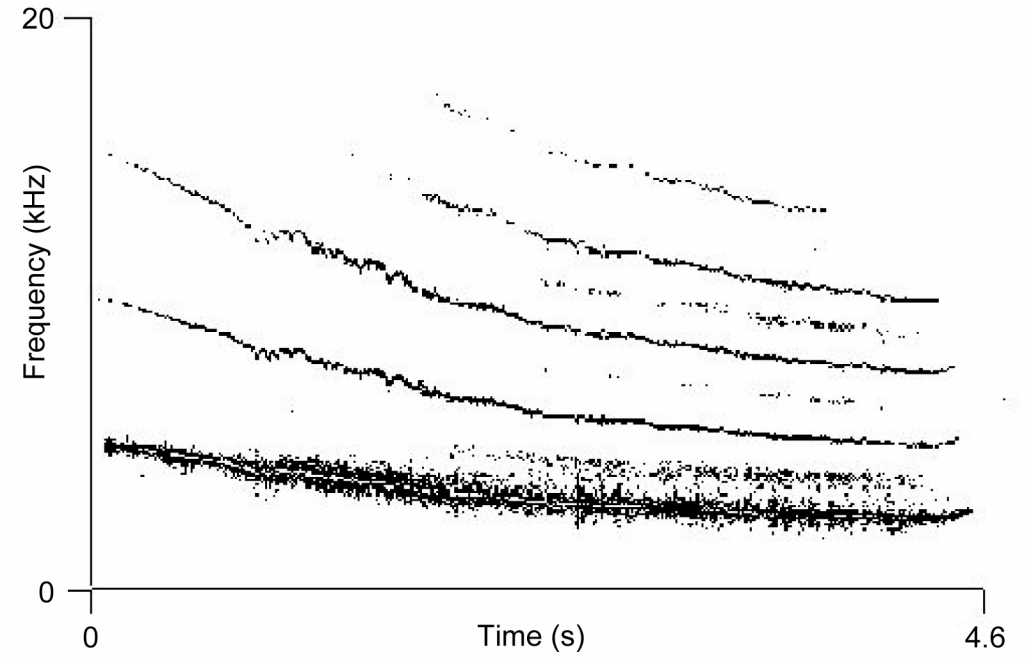
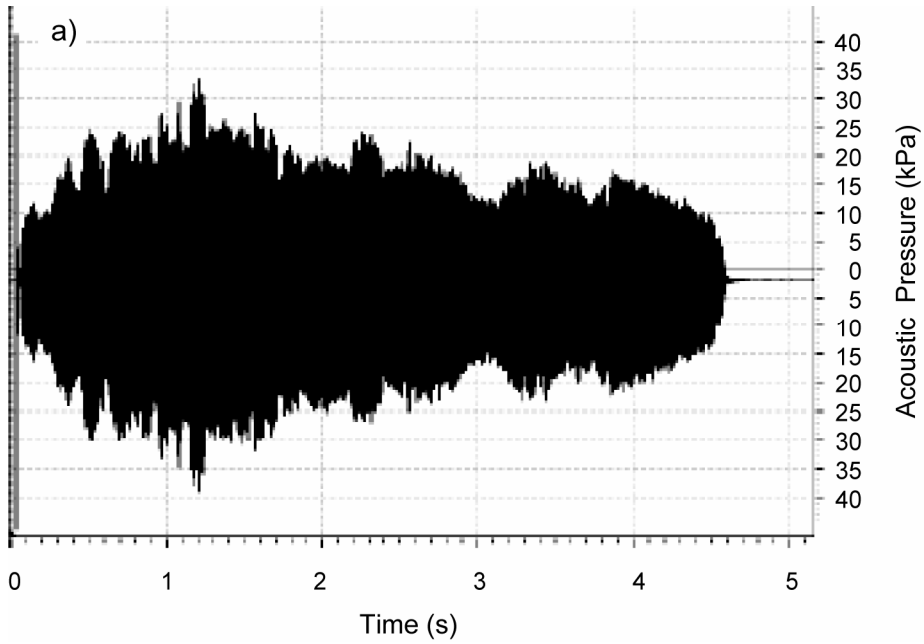


Figure 2. Spectrogram of whistle output, showing the peaks of the whistle spectrum as a function of time. The lowest line represents the first harmonic, or the fundamental, and the upper lines represent the higher harmonics.

There appears to be some confusion about such a model in the literature, where an open organ pipe model was suggested by Maxwell.[2] The open organ pipe model represents a half-wave resonator with two low impedance boundaries[3] where the ratio of the frequencies of the upper harmonics and the fundamental follows a simple 1, 2, 3, 4, ... relationship, termed here as the modal ratio. While the experimental data show such a relationship between the mode frequencies (see Figure 2), it does not fit the half-wave resonator model, which yields unrealistically low acoustic propagation velocities when calculated as the product of frequency and wavelength, with the wavelength equal to twice the effective chimney length. The modal ratio for a quarter-wave resonator, however, normally follows a 1, 3, 5, 7 … relationship, but it can be shown that non-linear distortions in the acoustic wave output are capable of producing the observed 1, 2, 3, 4 … modal ratios. So far, it has been found to be extremely difficult to account for the non-linear acoustic behaviour in the absence of suitable experimental measurement techniques capable of operating in a very hostile environment, and to simulate the process computationally would require considerable developmental effort. However, the simplified acoustic model still offers useful insights, particularly when the whistle chimney, or quarter-wave tube resonator, is considered as an acoustic wave trap. This helps to provide a better basis for understanding the possible effect of acoustic feedback on the chemical reaction rates in the whistle composition burn.

Experiments show that the whistle oscillations build up gradually after initiation.[3] It is presumed that before the periodic whistle noise is established, the initial pyrotechnic burn generates its own random noise, which is trapped by the whistle chimney and fed back towards the reaction front where it may be reinforced under favourable conditions. Therefore, the initial stage of the development of the oscillatory burn is considered to be a random process as shown in frame (b) of Figure 3, where random fluctuations precede the onset of coherent oscillations.



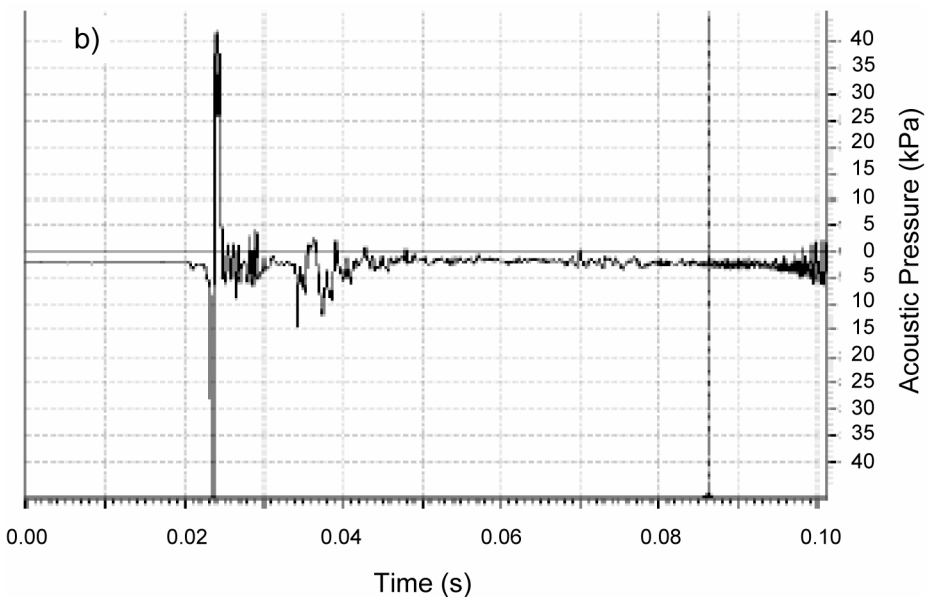


Figure 3. An example of the acoustic output of a pyrotechnic whistle device as a function of time with a vertical scale of approximately ±40 kPa. Frame a) shows the complete record of sound output of nearly 5 seconds duration and frame b) shows the first 0.1 s comprising an initial transient due to the electric match-head initiator, random reverberant sound decay, and onset of coherent narrow-band oscillations. Unsuccessful attempts at resonant feedback are evident from the random fluctuations just to the left of the cursor at approximately 0.087 s followed by the onset of build up in coherent whistle resonance.

The effect of the acoustic pressure on the reaction rate of whistling pyrotechnic compositions is not yet properly understood, but it is clear from the literature as well as experimental evidence that the acoustic pressure wave trapped in the chimney controls the combustion process. Moreover, the energy of the combustion feeds back positively into the trapped acoustic wave.

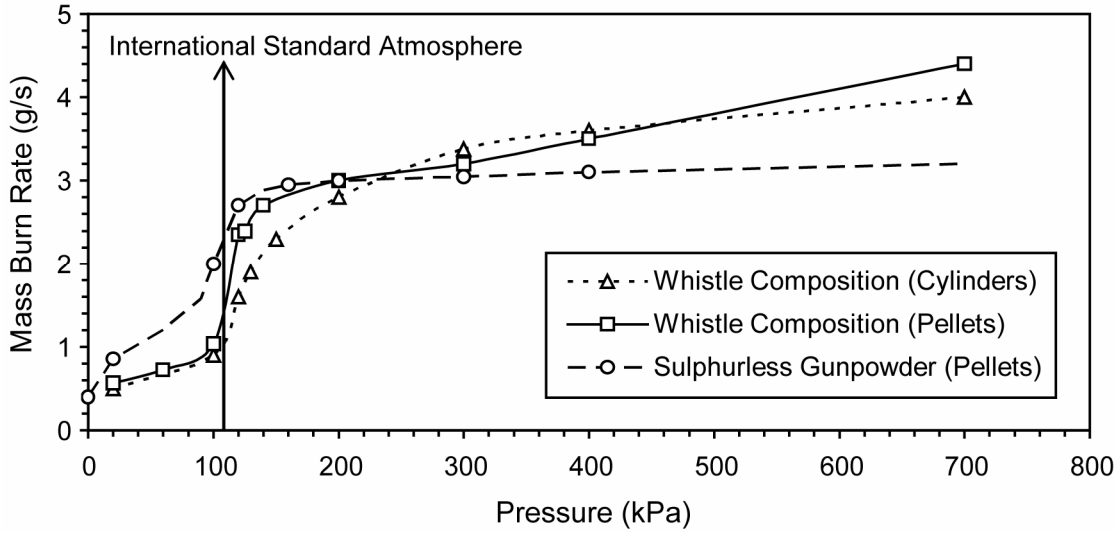


Figure 4. The relationship between static pressure (kPa) and mass burn rate (g/s) for whistle composition burning both as inhibited pellets in the open air, and at the bottom of open cylinders; in comparison to pellets of sulphurless gunpowder (Black Powder). The combustion of whistles ceased at pressures below 20 kPa, probably due to thermal losses from the burning front.

This process is sometimes called thermo acoustic feedback since the combustion is expected to impart energy to the acoustic wave through the addition of heat. The wave-trap model highlights one feature, which may be of considerable significance in the acoustic control mechanism of the combustion, namely acoustic pressure doubling at the reaction front. In the model, as portrayed in Figure 1, a compressional pulse is generated at the reaction front and propagates towards the chimney mouth where it is reflected, but proceeds as a rarefaction pulse of somewhat diminished magnitude back towards the reaction front. At the chimney mouth, the pulse magnitude becomes nearly zero due to the low acoustic impedance boundary condition, and all of the potential energy of the pulse is momentarily converted into kinetic energy. During this reflection process, some of the pulse energy is dissipated through acoustic radiation into open space. At the reaction front, the rarefaction pulse is reflected and its pressure magnitude is momentarily doubled because of the high acoustic impedance at the reaction front boundary. The doubling is due to conversion of all of the kinetic energy of the pulse into potential energy while in the rebound phase. The pulse then reverts to its previous magnitude (assuming zero losses) and proceeds back towards the chimney mouth. There it undergoes a reflection as described previously, but now it returns as a compressional pulse to the reaction front and completes the cycle, doubling temporarily in magnitude during the rebound phase.

3.1. Thermo Acoustic Feedback Mechanism

To build up oscillations in the pyrotechnic whistle device, a mechanism must exist that periodically adds energy to the trapped acoustic wave. Rayleigh[4] stated that vibrations in a resonant column might be generated through periodic addition of heat in phase with pressure wave condensation (compression). In an attempt to understand how this energy is imparted by the combustion process, the relationship between pressure and reaction rate was considered. Maxwell[2] asserted that the rate of burning of whistle compositions is not abnormally sensitive to pressure and that the acoustic pressure fluctuations do not appear to change the reaction rates sufficiently to account for the observed acoustic power of whistling compositions. These assertions are supported by the data (reference 1) set out in Figure 4, which demonstrate that pressure fluctuations about the atmospheric mean of 100 kPa of absolute pressure produce little more than a six-fold difference in average mass burning rate. Note that gun powder (Black Powder),

which produces a similar volume of permanent gas as whistle composition (~300 L/g), exhibits a similar increase in the mass burn rate with pressure, but does not exhibit oscillatory burning.[1]

Based on experimental observation and the above acoustic wave-trap model, it is believed that the acoustic pressure doubling at the reaction front controls the reaction process through thermochemical switching. It is suggested that acoustic pressure wave doubling at the reaction front is able to influence the temperature and pressure in the reaction zone and lead to differential fuel and oxidant decomposition rates. Thermochemical analysis of whistle fuels and oxidants by Wilson[1] showed that lowering of reaction temperature in a whistle composition is expected to lead to decreased decomposition rate of the oxidant while the fuel decomposition rate may continue relatively unabated. According to Wilson the layer of aromatic fuel thermally decomposes, producing solids and combustible gases including hydrocarbons and a highly reactive form of carbon. Thus, a doubled rarefaction pulse at the reaction front may lower the temperature and pressure at the reaction front and hence increase the net production of secondary fuels while decreasing the oxidant decomposition rate. A one half-cycle later, the doubled compression pulse will increase the temperature and pressure at the reaction front with a concomitant increase in the decomposition rate of the oxidant. The resultant combustion will be more energetic than in the preceding half-cycle and is therefore capable of adding energy to the acoustic wave, meeting the Rayleigh criterion. A build-up in the acoustic pulse height is possible via this mechanism with increasing contrast between the decomposition rates of the fuel and oxidant as the pulse height increases. In a fully developed oscillatory burn, the occurrence of distinct alternating half cycles of active and quiescent phases would be expected. Such behaviour was observed in experiments involving the recording (at 12,000 pictures per second) on a Kodak SP 2000C high-speed video system of combusting whistle devices pressed into transparent test blocks (see Figure 5).[1]

Maxwell demonstrated that the acoustic frequency of a pyrotechnic whistle decreases as the length of chimney above the burning front increases.[2] A series of experiments with 0.45 m long chimney extensions was designed to reduce the oscillation frequency to enable the combustion process to be more effectively recorded on high-speed video. The records of these devices exhibited a very clear distinction between the active (light) and quiescent (dark) phases of the combustion cycle as seen in Figure 6. Maxwell also made similar observations using streak camera photography.

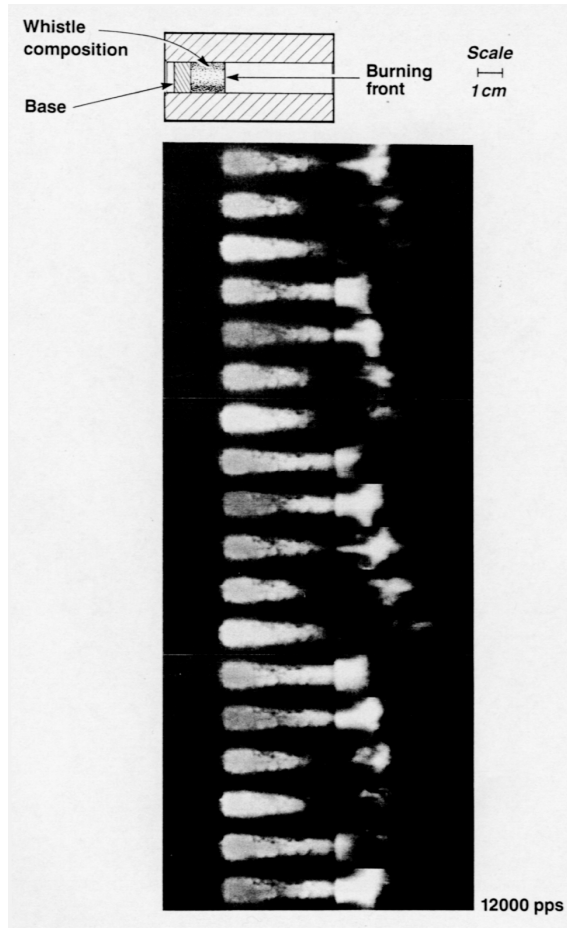


Figure 5. High-speed video record of a burning (3 kHz) whistle device showing combustion cycle 'switching' at the burning front.

It should be noted that during the dark period, the reaction is not extinguished, but is sustained, possibly as a smouldering process of hot carbon particles in an oxygen deficient, low-pressure environment. If the environmental temperature were to fall below that at which the fuel decomposes, the combustion reaction would likely be extinguished. This probably explains

why the whistles would not burn reliably at pressures much below atmospheric values, as indicated in Figure 4.

3.2 Quantitative Analysis of Acoustic Data

Useful information can be obtained from quantitative analysis of the acoustical data, such as acoustic pressure levels generated at the reaction front of a whistle device and specific impulse output, when compared with other energetic materials. The acoustic output of experimental whistle devices was measured (reference 1) with a Bruel and Kjaer Impulse Precision sound level meter located at a safe distance from the chimney mouth, and the sound pressure levels at the chimney mouth were calculated according to spherical spreading law. The acoustic pressure levels at the reaction front may be estimated from the acoustic properties of the chimney, considered here as a closed-open cylindrical waveguide. A more detailed derivation has already been performed in reference 1 so this study only considers some of the pertinent data and results.

In most of the experiments, the sound pressure level (SPL) was measured at a distance of one metre from the mouth of the whistle, with the SPL meter positioned at right angles to the whistle body. The initial chimney length, L, was 19.5 mm and the bore diameter, d was 12.5 mm. To calculate the effective wavelength, λ, of the wave trapped in the chimney, an end correction was applied to L so that

$$\lambda = 4L + 1.2\,d \cong 93 \text{ mm}$$

For the MRL(X) 418 whistle composition, the starting frequency was a little over 5 kHz and the recorded acoustic pressure waveform was nearly sinusoidal. Using the standard definition of SPL, the recorded waveform was converted to sound pressure and the spherical spreading law was applied to deduce the pressure amplitude just outside the chimney mouth. To calculate the pressure amplitude within the chimney, it is necessary to apply a transfer factor based on the reflection coefficient at the chimney mouth. This is called the resonant amplification factor (RAF), which determines the required build-up of internal wave amplitude until the acoustic energy imparted by the combustion is equivalent to the acoustic energy radiated from

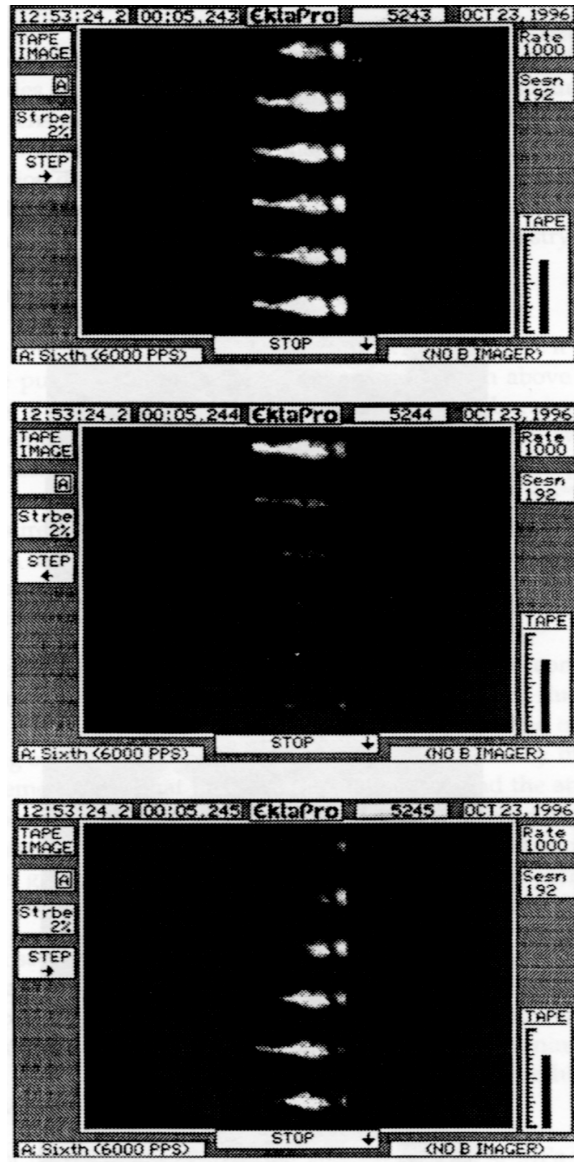


Figure 6. High-speed video record of a low frequency pyrotechnic whistle, showing the active (bright) and quiescent (dark) combustion cycles. To slow the whistle frequency to enable a full cycle to be recorded, an extended chimney tube was fitted to the device. When, in another experiment, a 'normal' 3 kHz whistle was located and ignited at a distance of 15 mm from the end of the low frequency whistle, pointing directly at the mouth of the extended tube, the combustion frequency of the first whistle was observed to increase.[1] This experiment demonstrated that the whistling frequency is controlled by the incoming pressure pulses (normally as a result of reflection from the tube mouth).

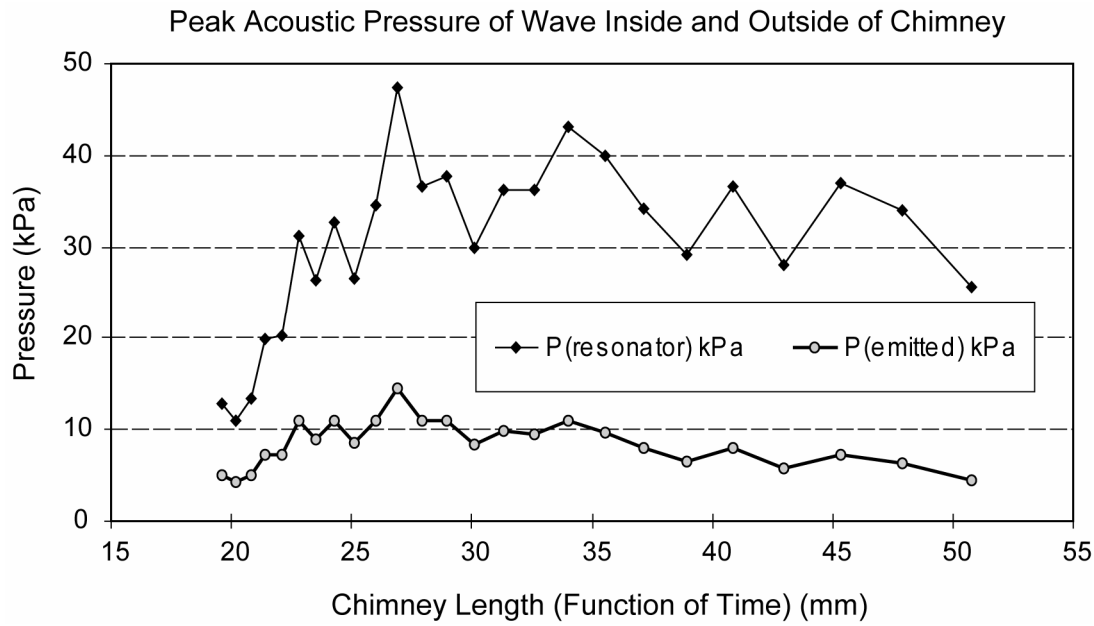


Figure 7. Translation of peak acoustic pressure for waves radiated from the chimney ($P_{emitted}$) to peak pressure for waves trapped inside the chimney ($P_{resonator}$). The translation is a function of chimney length, which varies with time as the whistle composition is consumed, and is governed by RAF (the resonant amplification factor).

the chimney mouth. The RAF may be derived from first principles using acoustic theory for waves radiated from open cylinders, assuming no acoustic losses except by radiation from the chimney mouth. Adopting the approach and formulation of Fletcher and Rossing,[3] it is found that the RAF varies linearly with chimney length, starting at a value of 2.5 at the beginning of the burn, and closing at a value of about 6 at the end of the burn.

Figure 7 shows an approximate RAF translation between internal and external peak pressure for the same sound-pressure record as depicted in Figure 3. This illustration raises two important issues:

1) The internal wave amplitude is vacuum limited (i.e., it cannot exceed 50% of ambient pressure). Otherwise, pressure doubling at the reaction boundary during the rarefaction phase would demand negative pressures, which cannot be physically achieved. Hence, at atmospheric pressure, the amplitude is limited to about 50 kPa.

2) As the chimney length increases, the RAF increases, and therefore, the maximum possible output of the whistle decreases because of the vacuum limit. For the experiments with 0.45 m extensions, the RAF ≅ 50 and the expected maximum amplitude radiated from the chimney would be of the order of 1 kPa only. This corresponds to a 20-fold reduction in amplitude, or a drop of about 25 dB in sound output.

4. Energetics

4.1 Acoustic Impulse

Normally, pyrotechnic compositions are designed to burn at a relatively slow rate to produce the required physical effect (e.g., light, smoke, heat, gas or a delay interval). This is usually achieved by a combination of ingredient selection and formulation, and by either pressing or casting the composition into a container so that propagation proceeds by inherently slow layer-to-layer thermal processes. In certain cases, however, the burning rate must be greatly increased to produce the required effects.

In the case of photoflash compositions, where a pulse of light, sound and smoke must be produced in a very short time (e.g., in a spotting

charge for an artillery shell), the composition is filled as a loose powder into a container; greatly increasing the surface area available for combustion. The container provides a level of confinement, which serves to increase the internal pressure rapidly. The high thermal output of photoflash compositions (over 8 kJ/g, compared with gun powder (Black Powder), approximately 3 kJ/g) is a result of the use of metallic fuels and this, in conjunction with the other factors, produces a fast reaction rate (often several hundreds of metres per second) and high pressures. The reaction proceeds throughout the void spaces present in the filling and the entire mass of composition combusts, virtually simultaneously. The container ruptures and a single, high amplitude acoustic impulse is produced. Hitherto, the deflagration of loose, metal-fueled photoflash compositions has been regarded as probably the most energetic of the more common pyrotechnic sound-producing reactions when considered on a mass for mass basis.

To compare the acoustic output of loose-filled photoflash composition with loose-filled whistle composition, cardboard-cased test charges were prepared, each containing 50 mg of:

- the magnesium fueled photoflash composition MRL(X) 206, which contains 40% magnesium, 59% potassium perchlorate, and 1% acaroid resin and
- the whistle composition MRL(X) 418.

The electrically-initiated charges were tested for acoustic output; the specific impulse produced by the charges was 1.1 and 0.76 Pa s/g, respectively. Because the positive phase duration of the events were similar, the value produced by the whistle composition can be considered as a surprisingly high result, given the non-metallic nature of its fuel. It is important to note that the specific impulse produced by a single active cycle at the reaction front of *consolidated* whistle composition is estimated to be about 3,500 Pa s/g (using an 11 kPa half-sinusoidal pulse, a frequency of 3,000 Hz and an average burn rate of 1 g/s).[1]

High amplitude, non-cyclic impulse sound can also be produced using primary explosives, but neither the container nor the need to use a loose filling is a critical requirement. This is because the propagation mechanism of primary explosives is often detonation resulting from the formation of a supersonic shock wave. However, Wilson[1] demonstrated that whistle composition, when initiated with a detonator, did not produce an indentation in the witness plate—a test designed to indicate the formation of a detonation wave.

Clearly, a pyrotechnic whistle device is a very efficient converter of chemical to acoustic energy, but the mechanism of sound production from the consolidated burning front within an open tube is evidently different (producing a greater acoustic impulse) from that when the composition deflagrates in the normal sound-producing mode (i.e., when filled as a loose powder and ignited under confinement).

4.2 The Consumption of Mass

The mass of the reactants involved in the production of each acoustic impulse in an operating whistle device would normally be expected to be determined by the area of the burning surface and the degree of thermal energy intrusion into the pressed compact ahead of the reaction front (which is in turn determined by its gas permeability). However, under examination, pressed whistle compositions exhibited very low void spaces,[1] a characteristic likely to limit the mass of composition available to contribute to each acoustic impulse. The mass burning rate figures quoted in this work for whistling MRL(X) 418 are average values; that is the sum of the mass required to produce the acoustic impulses and the mass consumed during the quiescent periods per second. It has been demonstrated (Figure 4) that the mass burning rate of a 12.5 mm calibre, 3000 Hz whistle functioning at ambient pressure is about 1 g/s and that the lowest mass burn rate at which linear combustion is reliably sustained is about 0.5 g/s. But, even if it is assumed that during the quiescent interval, the mass consumption rate is zero (e.g., a 'smouldering' reaction of hot carbon particles) and that virtually all the available mass of whistle composition is required to produce the observed acoustic pulse, each single acoustic impulse consumes a maximum of only $1/3000 = 3.3 \times 10^{-4}$ g of composition. This mass, burning as a reaction between discrete fuel and oxidiser particles, appears much too low to account for the observed acoustic power.

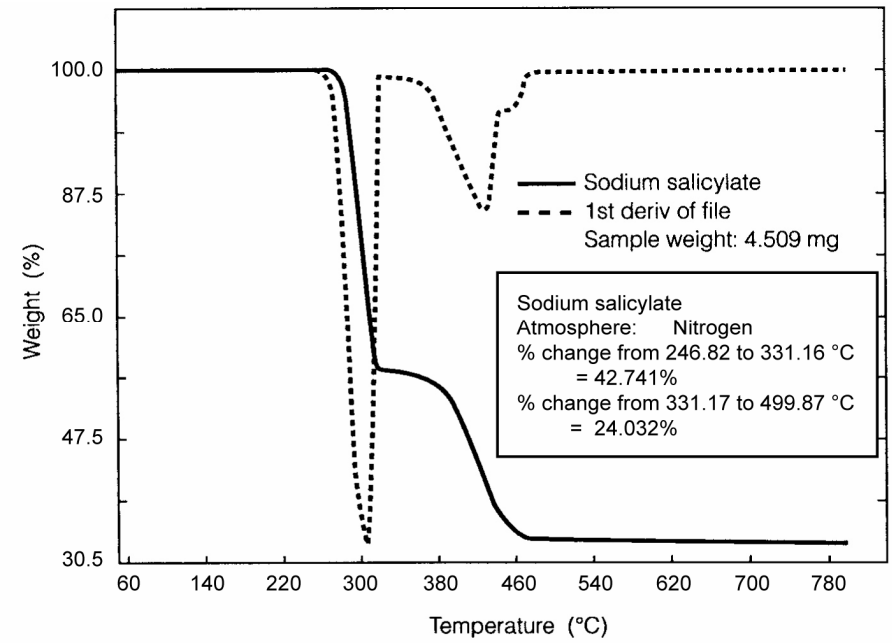


Figure 8. TGA of sodium salicylate. The analysis reveals a two-stage decomposition process commencing at approximately 250 °C.

From the foregoing, pyrotechnic whistles are unusual as acoustic impulse generators in that:

- whistle compositions contain an organic fuel (which would be expected to produce a low combustion temperature and resultant pressure),
- a higher acoustic impulse is produced from the reaction front of a functioning whistle compact than from a greater mass of the same composition ignited as a loose filling under confinement,
- whistle compositions are unlikely to propagate by a cyclic detonation mechanism (inferring a relatively slow reaction rate), and
- the very small mass of reactants consumed to produce each acoustic impulse would likely preclude a simple combustion process involving solids.

4.3 Fuel and Oxidiser Decomposition Temperatures

Thermo gravimetric analyses (TGA) of a typical whistle fuel ($NaC_7H_5O_3$ – Figure 8) and oxidiser ($KClO_4$ – Figure 9) were conducted to determine the relative onset decomposition temperature of the ingredients.

At the relatively slow heating rate of the thermal analysis instrument (40 °C/min), the results indicate approximately a 350 °C disparity between the onset decomposition temperatures of the whistle fuel and oxidiser. While the values of the decomposition temperatures of the individual ingredients may change—both when slowly heated as a pyrotechnic mixture in the TGA instrument and when heated at the greater rate experienced in a burning whistle—it is unlikely that the ingredients will decompose at precisely the same temperature. It has already been demonstrated that, within a burning whistle tube, the pressure level varies greatly with time; this would likely lead to concurrent temperature fluctuations between the active and quiescent cycles and slightly disparate ingredient decomposition times. The fuel would continue to decompose in a low pressure and low temperature environment, while the oxidiser

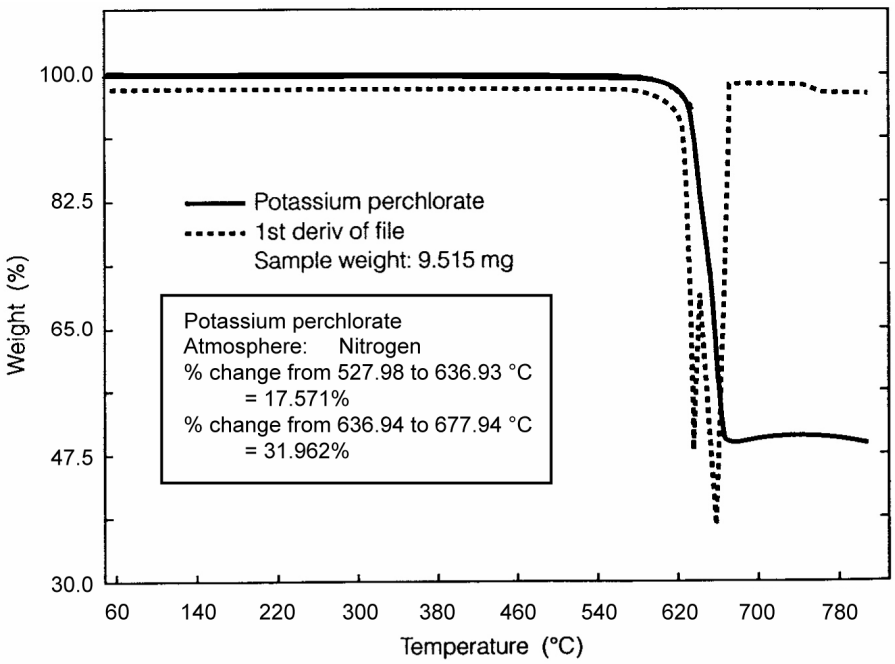


Figure 9. TGA analysis of potassium perchlorate showing onset decomposition temperature at approximately 600 °C.

component would not fully decompose until the incoming pressure pulse had sufficiently raised the temperature of the reaction front.

4.4 Decomposition Products

An experimental analysis of the thermal decomposition of selected whistle fuels in a reducing atmosphere has been performed by Wilson.[1] The dehydration reactions indicated the formation of highly energetic fuel species (confirmed by the explosion of several of the reaction vessels that had likely admitted air during the experiment). While this phenomenon has not been directly observed at the combustion front of a whistle device, it is thought to be a key factor resulting from the oscillating burning environment in whistle compositions. The observation that the whistle fuels exhibit a lower onset decomposition temperature than the ignition threshold temperatures of their pyrotechnic compositions suggests that the physico-chemical properties of the fuels might be altered within the reaction zone, immediately before ignition of the fuel–oxidant mixture occurs. This is not necessarily an uncommon phenomenon in pyrotechnics technology and can normally occur as an ongoing process just ahead of the combustion front as the reactants are preheated as a result of the permeability of the compact, particularly when combustion occurs under pressure.[5] Consolidated whistle compositions, however, have been demonstrated to exhibit very low permeability, probably due to the physical properties of the aromatic fuels.[1] This would restrict the mass of reactants involved to a thin layer on the surface of the consolidated compact.

Thermal decomposition analyses in reference 1 indicated the presence of the following combustible volatiles for potassium benzoate ($KC_7H_5O_2$): CH_4, C_2H_4, C_2H_6, C_3H_8, C_4H_{10}, C_6H_6, CO, and for sodium salicylate ($NaC_7H_5O_3$): CH_4, C_2H_4, C_2H_6, C_3H_8, C_4H_{10}, C_6H_6, CO, C_6H_5OH. The relative abundance of these species varied with decomposition temperature, and the reader is referred to reference 1 for complete details. It is important to note, however, that the presence of approximately 40% by mass of elemental carbon or carbon compounds was found in the condensed residue. The residue was examined under a Scanning Electron Microscope (SEM) and this revealed that in the condensed state, the residue is mostly carbon and takes the form of spheroids of approximately 1μm diameter (Figure 10).

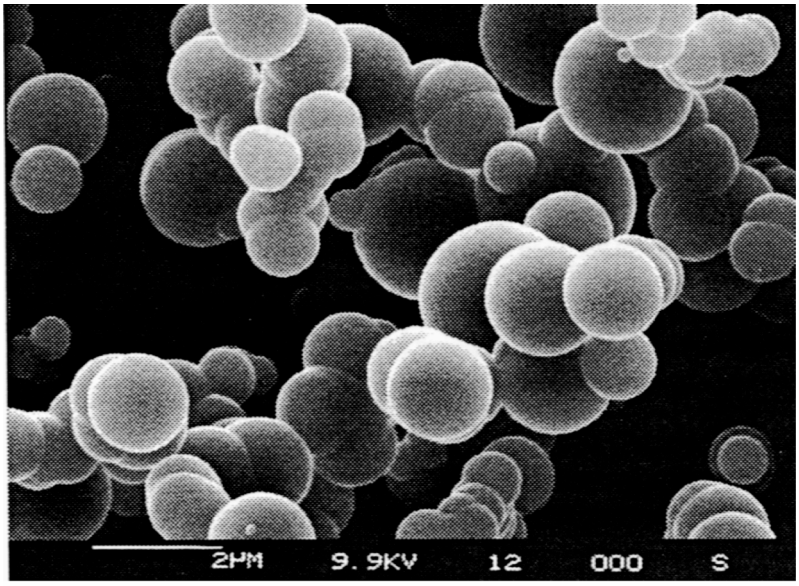


Figure 10. SEM of carbon spheres resulting from the thermal decomposition of whistle fuel in a reducing atmosphere. Crushing the spheres revealed that they were hollow.

Mechanical compression of the carbon spheres has provided strong evidence that at least some of them are hollow. This leads to speculation regarding the dynamics of the formation process and the nature of the gas species that may fill the spheres. The actual form that carbon takes at the moment of the destruction of the aromatic ring at the elevated temperature of the combustion front in a pyrotechnic whistle can only be guessed at, but it is probable that it is in a finely divided state. This hot and highly reactive carbon, together with any combustible gases, which form from the aromatic fuel, would represent a new and relatively energetic fuel mixture. This, when burning under pressure in the oxygen gas resulting from the thermal decomposition of the oxidiser, might account for the observed acoustic efficiency and explosive power of pyrotechnic whistles.

4.5 Explosive Behaviour

The proposed ability of whistle compositions to form a highly reactive fuel–oxygen mixture under certain conditions of temperature and pressure might also explain their tendency to occasionally explode violently, for example when accidentally ignited as a loose powder at the bottom of a filling funnel or as a result of the 'flash down the side' phenomenon in a functioning whistle device (see reference 1). In both these circumstances, the mass of reactants is uncontrolled by the normal constraints of a finite and consolidated reaction layer, and a limited combustion pressure environment. Under uncontrolled conditions, the production rate of the energetic fuel species and oxygen would likely become exponential—resulting in the observed explosions.

So far, experimental evidence and some theoretical considerations have lead to the conclusion that the participation of acoustic stimuli in the explosive failure of pyrotechnic whistles is unlikely. The acoustic waves tend to quench the linear combustion rate of whistle compositions and although more reactive fuel species may be created during the quiescent phase of the oscillating burn, they would normally be produced in small discrete quantities before being consumed in the active phase of the combustion cycle.

The role of higher harmonics as stimulants for runaway reactions is virtually ruled out. First, the upper harmonic components are usually weak, and second, only the odd harmonic components are able to physically participate in the reaction control in a quarter-wave resonator. In practical whistle devices, such components

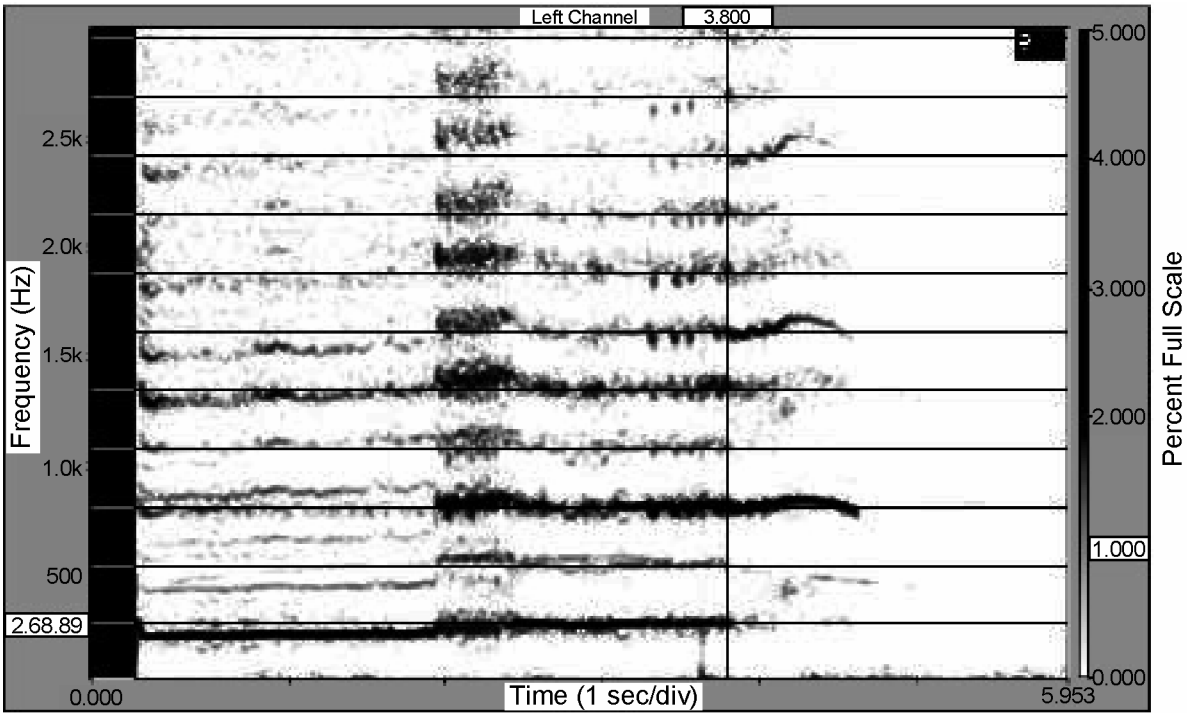


Figure 11. Spectrogram of whistle output for an experiment with a 450 mm chimney extension. It shows the peaks of the whistle spectrum as a function of time and a harmonic cursor has been laid over the temporal spectrum lines. The first harmonic frequency is at approximately 270 Hz. A strong switch to oscillation at the third harmonic frequency is evident at the 2 s marker, and at 3.8 s (position of cursor) the first harmonic is extinguished while the third harmonic component continues—together with its non-linearly generated overtones—until the composition has burnt out.

will be well above the critical cut-off frequency of the oscillatory burn and will therefore be excluded. However, in experiments with chimney extensions, where the fundamental burn frequency (approximately 270 Hz) was well below the cut-off frequency, switching of the burn oscillations to third harmonic frequency was evident (see Figure 11) and consistent with the model. The switch to a higher mode frequency did not result in runaway reaction, though, and the behaviour could probably be described as preferential mode competition.

Other experiments, in which strong tonal acoustic stimuli were externally applied to functioning whistles, demonstrated an effect on the reaction rate, but only by way of disrupting or altering the control cycle.[1,6] Similarly, experiments with externally applied acoustic shock stimuli have not had a detrimental effect on safe whistle performance, indicating that acoustic pressures are unlikely to induce fragmentation of the fuel–oxidiser compact.

5. Concluding Remarks

The acoustic model shows that acoustic pressure doubling at the reaction front may be critical to the coupling between acoustic waves trapped in the whistle chimney and the combustion process. Temperature and pressure switching is believed to control the decomposition rates of the whistle fuel and oxidant resulting in a two-stage combustion cycle. The first, quiescent stage, involves the decomposition of fuel to form highly reactive species in an oxygen poor atmosphere through acoustically lowered pressure and temperature. The second, active stage, involves the rapid combustion of the new fuel species in an oxygen rich atmosphere through acoustically elevated temperature and pressure. The energy released in the active cycle feeds positively into the acoustic wave trapped in the chimney, but its final amplitude will be governed by the balance of energy in-

jected by the combustion and the radiation and visco-thermal losses. Furthermore, the internal wave amplitude cannot exceed vacuum during the pressure doubling in the rarefaction phase, so this will be also a limiting factor in the acoustic output, particularly for long chimney lengths. However, further investigation (possibly assisted by sampling the combustion residues at the burning front from a whistle that has been 'switched off' by sudden exposure to vacuum) is required to validate the proposed combustion model before definite conclusions are drawn.

6. References

1) M. A. Wilson, *The Combustion and Explosion of Pyrotechnic Whistling Compositions*, Report DSTO-TR-0717, Aeronautical and Maritime Research Laboratory, Defence Science and Technology Organisation: Melbourne, Australia, 1998, 68 pp.

2) W. R. Maxwell, "Pyrotechnic Whistles," *4th Symposium on Combustion at MIT Cambridge*, Massachusetts, USA (1952). Reprinted in *Journal of Pyrotechnics*, Issue 4 (1996).

3) N. H. Fletcher and T. D. Rossing, *The Physics of Musical Instruments*, Springer Verlag: New York, 1991, 474 pp.

4) J. W. S. Lord Rayleigh, *The Theory of Sound*, Vol. 2, Dover: New York, 1945, 226 pp.

5) F. S. Scanes, "Thermal Analysis of Pyrotechnic Compositions Containing Potassium Chlorate and Lactose", *Combustion and Flame*, Vol. 23 (1974) pp 363–371.

6) J. A. Domanico, Technical Discussions. Edgewood Research, Development and Engineering Centre, Aberdeen proving Ground, Maryland, USA (1996).