Techniques for the Quantitative Analysis of Sulfur and Chlorate in Fireworks Compositions

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ABSTRACT

This paper examines the analysis of pyrotechnic compositions found in fireworks for the presence of sulfur and chlorate ion (ClO_3^-). Admixtures of these two components can produce compositions which have high sensitiveness to mechanical stimuli (e.g., friction and impact), may be thermally unstable, and are not normally permitted in fireworks in the UK. Analytical methods for the admixture have, in the past, been qualitative. Colorimetric techniques have been developed for the quantitative analysis of sulfur and chlorate which use readily available materials and equipment. The techniques have been validated by examining pyrotechnic mixtures with known proportions of sulfur and chlorate. Fireworks compositions have been analysed and varying levels of sulfur and chlorate found.

Keywords: sulfur/chlorate admixture, analysis, fireworks, sulfur, chlorate

Introduction

In the United Kingdom (UK) there has been a long standing prohibition of sulfur/chlorate admixtures in fireworks. Such admixtures are in contravention of Order in Council No. 15 of the UK Explosives Act[1] which prohibits "fireworks containing sulfur in admixture with chlorate of potassium or other chlorate, unless with the consent of and subject to conditions approved by a Government Inspector". This 1894 addition to the 1875 Act was the result of some twenty-eight accidents and eleven deaths which occurred in the period between the Act and the additional legislation and were attributed to sulfur/chlorate admixtures.[2]

During check examinations of fireworks, items may be found for which chemical analysis indicates sulfur/chlorate admixtures. In our work the presence of sulfur and chlorate in firework components was indicated by positive results in all tests described in the British Standard.[3] The methods are only qualitative, however, and need to be supplemented for enforcement or consent purposes by quick and reliable assessments of the levels of the two materials in fireworks compositions.

This paper describes the development and validation of methods to quantitatively assess sulfur and chlorate in fireworks and their component compositions by extending two tests given in the British Standard. The tests developed for quantitative analysis were the anilinium chloride test for oxidiser and the piperidine test for sulfur: both materials generate characteristic colours. In a similar fashion Urone and Bonde[4] have reported that chlorate in well waters could be determined by the colour generated from o-toluidine in concentrated hydrochloric acid.

Experimental

Mass measured during the course of this work can be traced to national standards. Milligram quantities were measured to 0.01 mg, and gram quantities were measured to 0.01 g. Volume measurements were made using Grade A volumetric apparatus, except for 500 µL quantities which were delivered using a fixed volume automatic pipette. Colorimetric measurements were carried out using a CO75 colorimeter (WPA) using gelatine filters with a typical bandpass of 40 nm. Although the methods have not been tested with other colorimeters or visible spectrophotometers, it should be

possible to adapt the techniques for use with other suitable optical devices.

Sample Preparation

A series of samples containing sulfur and an inert material, and chlorate and an inert material were prepared for the initial experiments. Salts, typical of firework compositions, were ground carefully in a clean agate pestle and mortar to form a fine powder and placed in a sample bottle for dispensing. Flowers of Sulfur (Timstar Laboratory Supplies Ltd.) were used as supplied. Specimen formulations were then prepared from dried salts, sulfur and inert material (e.g., talc and sodium chloride) by simple weighing and mixing within the sample tube. Typically 200 mg to 1g of material was prepared for analysis. In the early tests, the specimens were prepared without further additional treatment of the salts, but in later tests the salts were dried prior to specimen preparation.

Consolidated firework compositions were, generally, carefully pared to produce a fine powder for extraction. Where small hard grains were encountered, single grains were ground carefully in an agate pestle and mortar to produce fine powder. Firework compositions were analysed without drying to avoid heating potentially thermally unstable mixtures.

Analysis

The quantitative analysis of sulfur has been based on the colour generated by sulfur when it dissolves in piperidine. Sulfur concentration up to $0.85 \mathrm{~mg~cm}^{-3}$ could be measured using a 440 nm filter. Any sample having a greater concentration required dilution with piperidine before measurements could be made.

A stock solution of sulfur in piperidine was prepared by dissolving 50.51 mg of sulfur and making the solution up to $50 \mathrm{~cm}^3$ in a volumetric flask. A series of $500 \mu \mathrm{L}$ aliquots of the stock solution and piperidine were used to prepare a series of solutions containing a range of concentrations of sulfur from $0–0.85 \mathrm{~mg~cm}^{-3}$. Approximately $2.5 \mathrm{~cm}^3$ of piperidine was transferred to a $1 \mathrm{~cm}^3$ path glass cuvette and used as the reference solution. About $2.5 \mathrm{~cm}^3$ of prepared solution was placed into a clean rinsed cuvette, the clear surfaces wiped with tissue and an absorbance measurement taken. The procedure was repeated for the series of prepared solutions and the results were used to prepare a calibration curve and spreadsheet model.

A standardised method of extracting sulfur from prepared samples and firework compositions was developed. Consolidated firework compositions were, generally, carefully pared to produce a fine powder to aid dissolution of sulfur. In the case of Black Powder, single grains were very carefully ground in an agate pestle and mortar. Three portions of each sulfur-containing composition were taken and weighed in small sample bottles, 50×18 mm were found suitable. The samples had weights in the range 10–75 mg. A $5 \mathrm{~cm}^3$ aliquot of piperidine was pipetted into each sample bottle which was then stoppered. The samples were left for no more than 10 minutes to allow dissolution of the sulfur, which was aided by gentle shaking of the extract from time to time. After dissolution, the solutions were filtered using tissue- or cotton-plugged dropping pipettes and run into clean sample bottles.

About $0.5 \mathrm{~cm}^3$ of each filtered piperidine solution was used to rinse cuvettes prior to analysis. Then $2–3 \mathrm{~cm}^3$ of the filtered solution was transferred into the rinsed cuvette for absorbance measurement. If the absorbance was on-scale, this value was used directly for calculation. When the solution was too concentrated, it was diluted. To dilute the sample $500 \mu \mathrm{L}$ aliquots of the filtered piperidine extract were transferred into a clean sample bottle and $500 \mu \mathrm{L}$ aliquots of piperidine added. The dilution factor required for a particular extract was found by trial and error, but generally $3–4 \mathrm{~cm}^3$ of diluted sulfur extract was produced.

Colorimetry was performed on each of the three extracts to obtain a mean sulfur content of the sample.

It is important that samples are analysed before the yellow colour starts to fade. The colour change was found to be slow. Normally, samples were analysed within 5–10 minutes of extraction.

The quantitative analysis of chlorate has been based on the colour generated by the anion when it reacts with anilinium chloride (aniline hydrochloride). Chlorate solutions with a concentration up to $2 \, mg \, cm^{-3}$ could be measured using a 680 nm filter. If a greater concentration of chlorate was obtained in the primary extraction, dilution of the sample was required.

A stock solution of approximately 0.2% potassium chlorate in water was made by dissolving 0.2003 g of dried potassium chlorate in distilled water and making the solution up to $100 \, cm^3$ in a volumetric flask. A series of solutions containing different concentrations of chlorate in the range $0–2 \, mg \, cm^{-3}$ was prepared by taking 500 µL aliquots of the stock solution and distilled water. A set of $5 \, cm^3$ portions of 5% anilinium chloride (technical grade aniline hydrochloride) in 8M hydrochloric acid were placed into test tubes; $150 \times 20 \, mm$ tubes were found suitable. About $4 \, cm^3$ of anilinium hydrochloride solution was placed in a disposable plastic cuvette and used as reference. The colorimeter was set to kinetic mode to measure maximum absorbance from the chlorate-anilinium chloride reaction.

A 500 µL portion of the 0.2% chlorate solution was transferred to a test tube containing $5 \, cm^3$ anilinium chloride solution using an automatic pipette. The solution was rapidly shaken to ensure mixing and about $4 \, cm^3$ transferred into a clean, plastic cuvette. The cuvette was placed in the colorimeter and the absorbance monitored. The maximum absorbance reading was recorded. It was found that the maximum absorbance occurred within 1 minute of mixing. Samples of chlorate which had been diluted were similarly treated using clean disposable plastic cuvettes for each measurement. The results were used to generate a calibration curve and spreadsheet model.

A standardised method for extracting chlorate from prepared samples and firework compositions was developed. Consolidated firework compositions were carefully pared to produce a fine powder to aid dissolution of any chlorate. Careful grinding of single grains could also be undertaken to pulverise any material which did not pare easily. A sample of the composition was taken and weighed in a small sample bottle; $50 \times 18 \, mm$ bottles were found suitable. Depending on sample size and chlorate proportion, a $2 \, cm^3$ or $5 \, cm^3$ portion of distilled water, was pipetted into the sample bottle which was then stoppered. The sample was left for up to one hour to allow dissolution of the chlorate, this was aided by gentle shaking of the extract from time to time. The samples had weights in the range 10–50 mg. When the chlorate had dissolved, the solution was filtered into a second sample bottle using a tissue- or cotton-plugged dropping pipette.

The colorimeter was set to kinetics mode and about $4 \, cm^3$ of anilinium chloride solution placed in a clean cuvette to act as a blank. A 500 µL aliquot of the extract was added to $5 \, cm^3$ of anilinium hydrochloride solution. This was shaken and about $4 \, cm^3$ immediately transferred to a clean, disposable plastic cuvette. The cuvette was placed in the colorimeter and the maximum absorbance was measured and recorded. If the solution saturated the colorimeter, the remaining extract was diluted, until "on scale" readings could be obtained by taking 500 µL aliquots of extract and 500 µL aliquots of water. There was sufficient undiluted solution from a $2 \, cm^3$ extract for triplicate analysis by colorimetry.

The reproducibility of the method was established by taking mixtures containing potassium chlorate and sodium chloride. These were prepared by weighing portions of potassium chlorate, adding appropriate amounts of sodium chloride, and re-weighing. The mixtures, about one gram, were produced with approximate potassium chlorate proportions of 10, 20 and 50%. The mixtures were shaken for 5–10 minutes to attain an even distribution of the components.

Appropriately sized samples were weighed into a series of sample bottles and $2 \, cm^3$ (10% sample) or $5 \, cm^3$ (20% and 50% samples) of distilled water added to produce a solution with concentration "on scale" for measurement. After allowing 10–15 minutes for dissolution, the samples were analysed by the standard procedure.

Errors in Measurement

The errors in measurement are dominated by the colorimeter measuring a scale of 0–2 to the nearest 0.01 in the absorbance scale. This introduces a limit to the accuracy of calculation of the percentage sulfur or chlorate in a composition. Additionally, the accuracy varied depending on the sample size taken to attain an on-scale reading (either as a direct limit on the sample size or through dilution). At about 5% sulfur content the colorimeter step size is under 0.1 while at 30% the step size rises to about 0.3. Similar effects were seen with the chlorate analysis where the colorimeter step size was increased to 0.4 at 50% chlorate in a sample.

Results

A set of six dilutions of sulfur in piperidine were prepared and the absorbances measured to produce the calibration graph, shown as Figure 1. The best fit regression line through the origin was generated. This line gave a correlation coefficient (R^2) value of >0.99 indicating a "good fit".
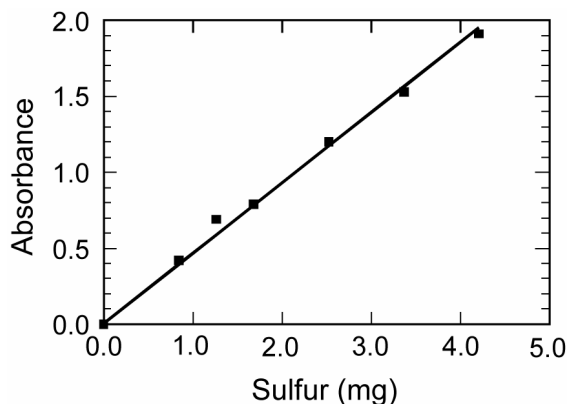

Figure 1. Sulfur calibration.

Reproducibility of the analysis for sulfur was examined using mixtures of sulfur in talc with approximately 5, 16 and 27% sulfur. The samples were analysed by the standard procedure and the results are reported in Table 1.

Table 1. Reproducibility of Sulfur Analysis.

Calculated % sulfur for 5.1% sample	Calculated % sulfur for 16.3% sample	Calculated % sulfur for 27.1% sample
4.9	15.3	27.6
5.1	15.2	27.0
5.0	16.0	27.1
5.0	16.9	26.6
5.1	16.1	27.9
5.3	15.3	27.1
4.7	16.0	26.8
4.8	24.0	28.1
4.9	16.3	28.1
5.0	15.1	27.0
Mean 5.0	Mean 16.6	Mean 27.3
Std. Dev. 0.2	Std. Dev. 2.7	Std. Dev. 0.6

Firework components were analysed and gave mean calculated sulfur contents of 3–30%, this is reported in Table 2.

Table 2. Sulfur Analysis, Firework Samples.

Sample	Extract	Calculated % sulfur	Mean (%)	Std. Dev.
Lift charge	A	9.5	10.2	1.0%
	B	11.0		
	C	10.9		
Flash composition	A	30.1	29.2	0.8%
	B	28.9		
	C	28.6		
Star outer composition	A	8.1	7.8	1.2%
	B	6.5		
	C	8.8		
Star inner composition	A	3.0	2.9	0.1%
	B	2.8		
	C	3.0		

In this study the amount of chlorate was calculated as the percentage of potassium chlorate, the most commonly used chlorate in fireworks. No tests have been performed on firework compositions to ascertain the presence of other chlorates.

A set of five dilutions was prepared and duplicate pairs of results used to generate the calibration graph shown in Figure 2. The best fit regression line through the origin was generated. This line gave a correlation coefficient (R^2) of >0.98 indicating a "good fit".
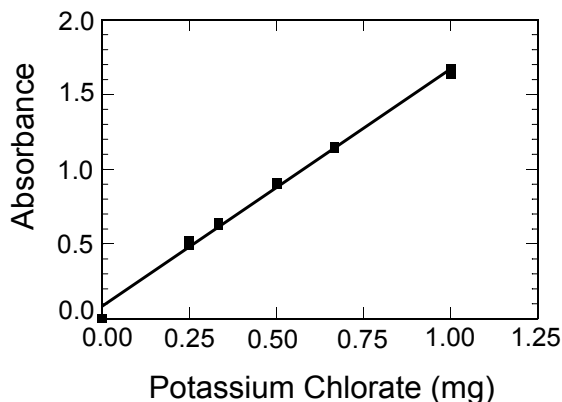

Figure 2. Chlorate calibration.

A series of three samples was prepared for the reproducibility testing. The samples contained 9.15, 19.7 and 50.2% potassium chlorate. The results of five sets of duplicate analysis are shown in Table 3. The levels of potassium chlorate derived from absorbance readings were found, within experimental error, to be in good agreement with the concentrations present in the dried samples. Additionally, as the proportion of potassium chlorate increased, there was a corresponding increase in the standard deviation. This is because, as the potassium chlorate proportion increases, a 0.01 change in absorbance registered on the colorimeter gave an increasing change in the potassium chlorate content.

Firework compositions containing chlorate were analysed following the standardised extraction procedure. Tests were carried out on firework composition without any drying. This was likely to underestimate the amount of chlorate, due to moisture uptake. Table 4 lists example firework compositions and their chlorate content. Chinese flash-banger composition, Flash composition in Table 4, was found to contain the highest proportion of chlorate, measured as potassium chlorate, at 46.2%.

Table 3. Reproducibility of Chlorate Analysis.

Calc. KClO$_3$ for 9.15% sample (%)	Calc. KClO$_3$ for 19.7% sample (%)	Calc. KClO$_3$ for 50.2% sample (%)
9.4	18.3	51.4
9.4	18.0	49.9
9.1	20.9	48.8
9.0	20.0	48.2
9.1	19.3	50.3
9.1	19.3	50.3
9.2	20.4	49.9
9.3	20.4	50.2
9.7	20.9	51.9
9.6	20.6	52.7
Mean 9.3	Mean 19.8	Mean 50.4
Std. Dev. 0.2	Std. Dev. 1.0	Std. Dev. 1.3

Table 4. Chlorate Analysis of Firework Compositions.

Sample	Extract	Calculated % KClO$_3$	Mean	Std. Dev.
Flash composition	A	46.1	46.2	0.2
	B	46.4		
	C	46.1		
Fuse composition	A	12.0	12.4	0.3
	B	12.6		
	C	12.5		
Star outer composition	A	11.4	11.2	0.2
	B	11.0		
	C	11.2		
Star inner composition	A	2.6	3.1	0.5
	B	3.4		
	C	3.4		

Discussion

Sulfur-containing samples for the reproducibility study were individually weighed from the solid mixture. It was anticipated that there could be variation in the sulfur levels found due to incomplete homogeneity. The 5.1% sulfur-containing sample give a mean value of 5.0% sulfur with a standard deviation of 0.2%. Problems with homogeneity were

encountered with the 16.3% sulfur-containing mixture, since the mean calculated sulfur content of 16.6% was achieved with six values below the sulfur percentage, three just over and a single value very much higher at 24.0%. This latter value was outside two standard deviations of the mean. The mixture for the third series of samples was ground in an agate pestle and mortar to ensure that any agglomeration of the sulfur was broken down and the material evenly mixed. The resulting calculated value of 27.3% was within experimental error (compared with the sample prepared at 27.1%) with no exceptionally high or low values. The standard deviation from the results was 0.6%

The extraction of sulfur from fireworks compositions depends on the state of the sample. Star compositions, for example, are consolidated into a hard solid mass, often with multiple layers. Initial separation of the layers may lead to contamination if the operator is not very careful. Once the material has been separated the sample will contain a mixture of fine and coarse particles. In practice, it is likely that all the material will be required for analysis. In the current study, star outer compositions yielded 10–15 mg of material for analysis from each star. For sulfur analysis this required one star per analysis. Thus there was the added possibility of some variation in composition between stars. For most compositions it was possible to obtain sufficient material to extract from fine particles. Re-extraction produced only the slightest trace of colour, indicating good primary extraction.

Lift charges in fireworks are often Black Powder. Lancaster[5] has reported that the usual composition for Black Powder contains 10% sulfur. Analysis of roman candle lift charges showed these to contain 10.2% sulfur. At this sulfur proportion the method is accurate to about 0.1%. A standard deviation of 1.0% is attributed to variation of composition within the samples. No investigation of the absorption of sulfur into charcoal during the extraction has been made. This could, in part, contribute to the variation in results.

Flash-banger composition may well contain sulfur. Weingart[6] reports one such composition for a "flash cracker" as having 30% sulfur

by mass. The flash composition tested in this program of work was found to have 29.2% sulfur. At this level a 0.01 change in absorbance results in a 0.2–0.3% change in estimated sulfur content.

Star compositions have also been found to contain sulfur. This is often incorporated to ease ignition.[7] The star inner composition analysed was found to contain 2.9% sulfur with a standard deviation of 0.1%. The outer priming composition contained about 8% sulfur with a standard deviation of 1.2% over the three extracts. Each star outer composition was pared from the inner composition and yielded only sufficient material for a single extraction. Thus each measurement represents the outer material from a different star. It is possible that star B outer contained a larger proportion of large particles from the paring, or was of a different composition. As the three stars had all originated from the same roman candle, it was thought that sample B had larger particles and was therefore not completely extracted in the time allowed before filtering and measuring the absorbance.

Chlorate analysis was performed by colorimetry. The method adopted was developed from the oxidiser test described in the British Standard. This spot test uses the blue colour produced by anilinium chloride in the presence of certain oxidisers. Common oxidisers found in fireworks are chlorates, nitrates and perchlorates. Of these only chlorate oxidises anilinium chloride in 8M hydrochloric acid. Other oxidisers that oxidise anilinium chloride and could interfere with the test are: permanganate, chromate and dichromate, peroxide and some other peroxy-salts.

Additional complication in the colorimetric method resulted from the kinetics of the reaction. In a typical analysis the blue colour developed over about one minute from addition of the chlorate solution and then slowly faded to a pale green. With vigorous mixing of the reagent and test solution and rapid transfer into a cuvette the maximum absorbance was found to be directly proportional to the concentration of chlorate in the test sample.

Firework samples were screened by using the chlorate identification test (i.e., an anilin-

ium chloride spot test followed by the confirmatory testing for halide, reducing the chlorate with sodium nitrite solution and retesting for halide). Due to the use of the oxidiser test as a basis for quantitative analysis it was felt necessary to always confirm the presence of chlorate before quantitative analysis was performed.

The reproducibility of the method was investigated with three mixtures containing 9.15, 19.7 and 50.2% potassium chlorate in sodium chloride. Mean potassium chlorate levels were measured and were within experimental error. As the concentration of chlorate increased the standard deviation also increased. This was attributed to the effect of the colorimeter step size since the absorbance is measured to two decimal places. The effect of this is a step size of 0.1 at 9.15% chlorate, 0.2 at 19.7% chlorate and 0.4 at 50.2% chlorate, for a 0.01 change in absorbance.

Flash-banger compositions used in fireworks normally contain chlorate or perchlorate with a fine metal powder, typically aluminium.[8] Chinese firecracker composition is reported by Conkling[9] to be a mixture of potassium chlorate, sulfur and aluminium. One such composition, described as Japanese "flash thunder" has potassium chlorate as 43% by mass. The flash composition tested had a potassium chlorate content of 46.2%.

Star compositions require the presence of chlorine in one of its oxidation states to form the coloured species SrCl or BaCl which generate red and green colours. Lancaster[10] reports both red and green stars to contain high proportions of chlorate in the composition. The Roman candle stars tested in the course of this work indicated 3.1% chlorate in the main star and 11.2% in the priming composition surrounding the body of the star. These stars had been declared as using perchlorate as oxidiser and chlorate should not have been present.

During check examination of fireworks, fuses were found to be the most common location for sulfur/chlorate admixtures. Analysis showed there to be 12.4% chlorate in what appeared to be a typical Bickford type fuse. It could be anticipated that this would be variable from batch to batch.

Conclusions

Previous examinations of fireworks for sulfur/chlorate admixtures have concentrated on identifying only the presence of these chemicals, not the amount. This was because of the absence of a quick and reliable quantitative method such as is presented in this paper. The development of a technique that can be used as a routine part of any sampling and testing campaign will enhance enforcement of the relevant legislation.

Routine quantitative analysis of firework compositions has not previously been available. The methods described in this paper should enable the levels of both sulfur and potassium chlorate in a firework composition to be assessed and distinctions to be made between different admixtures. Future work on the stability and reactivity of these admixtures may enable acceptable potential hazards to be estimated.

References

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