

Protocol for the full quantitative analysis of flash compositions

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Abstract. This paper describes a protocol for the full quantitative analysis of a flash composition. The protocol is based on the separation of the components by basic laboratory handling procedures as a first step. Subsequently, modern and routinely available instrumental analytics are used to quantitatively analyse the components. The protocol may easily be adapted to other pyrotechnic compositions such as whistle formulations or coloured star compositions. The method described here unequivocally allows the control of pyrotechnic mixtures for the absence of highly sensitive chemical combinations. The application of the protocol is demonstrated by the analysis of a flash composition which showed an unusual combustion behaviour. An unexpectedly large amount of silica has been identified to cause the observed properties.

Introduction

The analysis of pyrotechnic compositions is of interest for various reasons. For example, the detection of combinations of chemical components which are not permitted in several countries has widely been investigated. Spectroscopic methods such as Raman and InfraRed (IR) spectroscopy have been used to qualitatively identify oxidisers such as perchlorates, chlorates and nitrates directly in the composition.¹⁻⁴ Scanning Electron Microscopy with Energy Dispersive Analysis of X-rays (SEM-EDAX) has been used to directly identify various chemical elements and especially metallic fuels and sulphur.¹⁻⁴ After partial solvation of the composition, Ion Chromatography (IC) and Liquid Chromatography coupled with Mass Spectrometry (LC/MS) have been used to identify the oxidiser.¹ Other elements have been identified with Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES).¹ For the determination of sulphur and chlorate, quantitative protocols have been published, which allow determination of the exact amount of both components.⁵ Flash powder as a highly energetic composition is of special interest concerning the control of sensitive combinations, since several flash compositions containing sulphur and chlorate are well-known.⁵⁻¹⁰ IR spectroscopy and X-ray diffraction were used to monitor the aging of pyrotechnic compositions.¹¹

The residues and volatile substances emitted after combustion have been analysed by various analytical methods.¹²⁻¹⁵ Additionally, the combustion itself has been monitored by optical spectroscopy.¹⁶

Most of the analytical methods are used to qualitatively determine the presence or absence of a component. Only a few analytical approaches have been used to quantitatively determine the amount of one or two components.⁵ Recently, we were asked to analyse the flash composition of a small cylindrical ground salute. The pyrotechnic device explodes upon ignition with a deep sound and yellowish ball of flame untypical for flash powder, whereas performance and other characteristics match more with the presence of flash powder instead of black powder.

To unequivocally identify the mixture and to confirm the absence of prohibited and hazardous chemical combinations, we applied a protocol for the full quantitative determination of the composition (Fig. 1). The protocol is based on basic steps to separate the components of the composition and subsequently modern routine instrumental analytics available at virtually any chemical department.

A typical flash powder composition based on perchlorates, chlorates or nitrates as oxidiser and aluminium, magnesium or other metals and alloys

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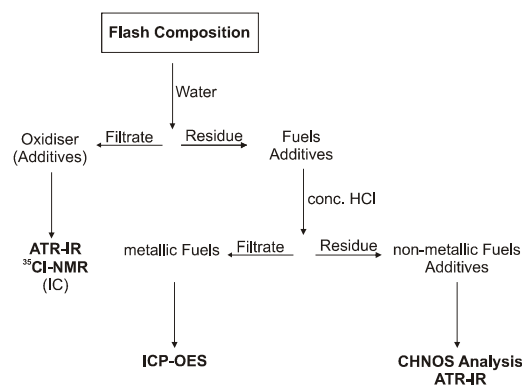


Fig. 1. Sketch of the basic analytical protocol.

as metallic fuels, sulphur and organic substances as non-metallic fuels and some additives has been assumed as a starting point.^{5,7-9,17}

Any black powder based composition or typical burst charge such as H3⁷ (contains chlorate) or KP⁷ (contains perchlorate) would be separated and identified by the given protocol as well.

The first step separates the water-soluble oxidiser from insoluble fuels (Fig. 1). The oxidiser is qualitatively determined by Attenuated Total Reflection IR spectroscopy (ATR-IR) as a method that is extremely fast and easy to handle. For the quantification of perchlorate, the scarcely used, though routinely available, fast and convenient ³⁵Cl-Nuclear Magnetic Resonance (NMR) spectroscopy is applied.

In a second step, (most) metallic fuels are dissolved in concentrated hydrochloric acid (HCl). The separated dissolved metal salts are quantitatively analysed by ICP-OES. This method provides information about virtually all conceivable metal ions that may be present in the sample.

The third step analyses the acid insoluble residue by classical elemental analysis to quantitatively determine organic fuels and sulphur. Additionally, ATR-IR spectroscopy is applied to check for residual additives.

The concept may be adapted for the full quantitative analysis of various other pyrotechnic compositions. For example, a typical whistle formulation based on perchlorate as oxidiser and an organic salt such as potassium benzoate as fuel^{7,8} may be quantitatively analysed with one single NMR sample and ¹H-/¹³C- and ³⁵Cl-NMR measurements. Non water-soluble oxidisers such as sulphates in unconventional flash mixtures¹⁸ or strobe compositions naturally would require a variation of the protocol.

Experimental

All quantities were measured to 0.1 mg after drying to constant weight. IR spectra were recorded on a *Bruker Alpha-T* FT-IR spectrometer equipped with a *Platinum diamond* ATR unit. NMR spectra were recorded on a *Bruker Avance III 600* (58.8 MHz (³⁵Cl)) FT-NMR spectrometer. Chemical shifts are given in ppm relative to KCl ($\delta = 0.0$). 1024 scans have been accumulated per measurement (30° pulse angle, RD = 0.25 s, LB = 5 Hz). For elemental analyses (CHNS) a *Vario EL, EAS* instrument (*Elementar Analysensysteme*) was used. ICP-OES analyses have been performed on a *Varian Vista MPX* instrument in 0.5 vol% HNO₃.

Sample preparation

A: A sample of 0.504 g of flash composition was stirred with 50.0 mL of warm deionised water. After filtration, the dark grey filter residue was dried. The solvent of the filtrate was removed with a rotary evaporator and the resulting white residue dried in a vacuum chamber. Filter residue: 0.215 g; remaining solid of filtrate after drying: 0.289 g.

6.3 mg of the solid after filtration have been dissolved in 750 μ L D₂O for ³⁵Cl-NMR measurement. For comparison, 6.3 mg pure KClO₄ (99%, *Sigma*) have been measured in 750 μ L D₂O, too. Six measurements have been averaged per sample. Integral of the corresponding signal at 1007 ppm: 108.0 \pm 1.3 (reference); 100.7 \pm 0.7 (sample). ATR-IR spectra have been measured as solid substance.

B: The filter residue (0.215 g) of step A has been stirred with 50.0 mL of 1% HCl for 1 min. After filtration, the dark grey filter residue was dried again. The solvent of the filtrate was removed with a rotary evaporator. Filter residue: 0.212 g. The remaining small amount of white solid after removal of the solvent of the filtrate was not dried further and digested with 25.0 mL of 0.5% HNO₃ for ICP-OES analysis. Main element found: Ca.

C: The filter residue (0.212 g) of step B has been stirred with 50.0 mL of 37% warm HCl for 10 h. After filtration, the light grey filter residue was dried again. The solvent of the filtrate was removed with a rotary evaporator and the resulting white residue dried in a vacuum chamber. Filter residue: 0.128 g; remaining solid of filtrate after drying: 0.686 g.

The filter residue was analysed by elemental CHNS analysis. Found: 68.4% S. The elements C, H, and N were below the detection limit. IR spectra have been measured as solid substance.

15.0 mg of the solid of the filtrate after drying were digested with 100.0 mL of 0.5% HNO₃ for quantitative ICP-OES analysis. Elements found: Al (16.3 mg L⁻¹), Ca (0.22 mg L⁻¹), Cr (0.003 mg L⁻¹), Cu (0.008 mg L⁻¹), Fe (0.1 mg L⁻¹), K (0.05 mg L⁻¹), Mg (0.1 mg L⁻¹), Mn (0.005 mg L⁻¹), Na (0.11 mg L⁻¹), Pb (0.02 mg L⁻¹), Si (0.18 mg L⁻¹), and Zn (0.018 mg L⁻¹).

Results and discussion

The small ground salute given for analysis contained a strongly confined net explosive quantity (NEQ) of 25 g. According to the general concept, a sample of 0.504 g of the composition was analysed. For the extraction of the oxidisers in water, a sufficient amount of water well above the solubility limit of potassium perchlorate (KClO₄) in water (1.7 g per 100 mL at 20 °C) was used. Other common oxidisers are significantly better soluble in water.

After filtration and removal of the water, 0.289 g of oxidiser (57% of the total composition) were obtained and analysed by ATR-IR spectroscopy (Fig. 2).

Clearly, the oxidiser consisted of KClO₄. The IR spectrum is completely congruent with pure KClO₄. Not the slightest indication for the presence of highly reactive potassium chlorate (narrow peak at 485 cm⁻¹) or the presence of nitrates is given. To quantitatively check if the oxidiser consists solely of perchlorate, the amount of perchlorate in a small fraction of the isolated sample was determined by ³⁵Cl-NMR (Fig. 3). The NMR spectrum of a sample of the oxidiser in deuterated water (D₂O) as NMR solvent revealed a single signal at 1007 ppm. This is consistent with the NMR signal reported for perchlorate.¹⁹ The integral

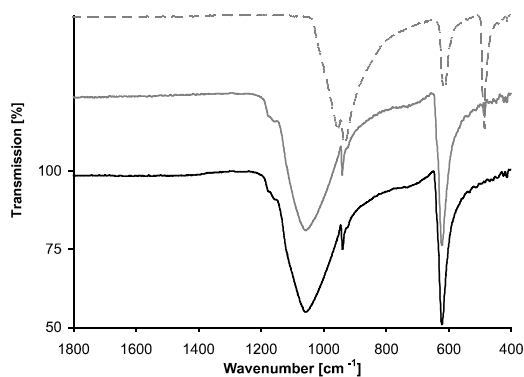


Fig. 2. ATR-IR spectra of potassium chlorate (top), potassium perchlorate (middle) and the isolated oxidiser (bottom).

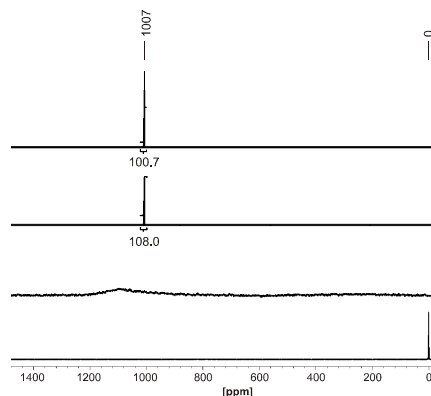


Fig. 3. ³⁵Cl-NMR spectra (from top to bottom): KClO₄, the isolated oxidiser, potassium chlorate (KClO₃) and potassium chloride (KCl).

of the signal in the NMR spectrum is directly proportional to the amount of dissolved material in a given volume of solvent. Comparing the value of the integral of the sample with a reference measurement which contained the same amount of pure KClO₄, a purity of >93% was revealed. Additionally, potassium was identified as the sole cation present by flame spectroscopy. Consequently, the oxidiser can be assumed to consist solely of technical grade KClO₄.

Unfortunately, chlorates do not show a narrow NMR signal suitable for quantitative analysis. The signal broadening is caused by a less symmetrical surrounding of the chlorine atom. Consequently, the quantification of chlorate or nitrate-based oxidisers requires other methods than ³⁵Cl-NMR for quantification, such as Ion Chromatography (IC).

The filter residue (0.215 g) after extraction of the oxidiser was assumed to consist of fuels and additives. In addition to the general concept, a first treatment with 1% hydrochloric acid (HCl) was applied (Fig. 4). Roughly 1% of the mixture was dissolved. The qualitative ICP-OES analysis revealed calcium as the main component. Consequently, 1% of calcium carbonate, which is readily dissolved by diluted acids, is assumed to be present in the composition. Calcium carbonate and other carbonates are commonly used as additives especially to stabilise sulphur containing compositions. Mainly, they neutralise potential acidic residues.^{9,17} The remaining 0.212 g of fuels and additives were stirred for several hours in warm 37% HCl to dissolve metallic fuels. After filtration and removal of the water, 0.686 g of metal chlorides were obtained. A sample of the metal salts was analysed by quantitative ICP-OES and was found to consist solely of aluminium (95%

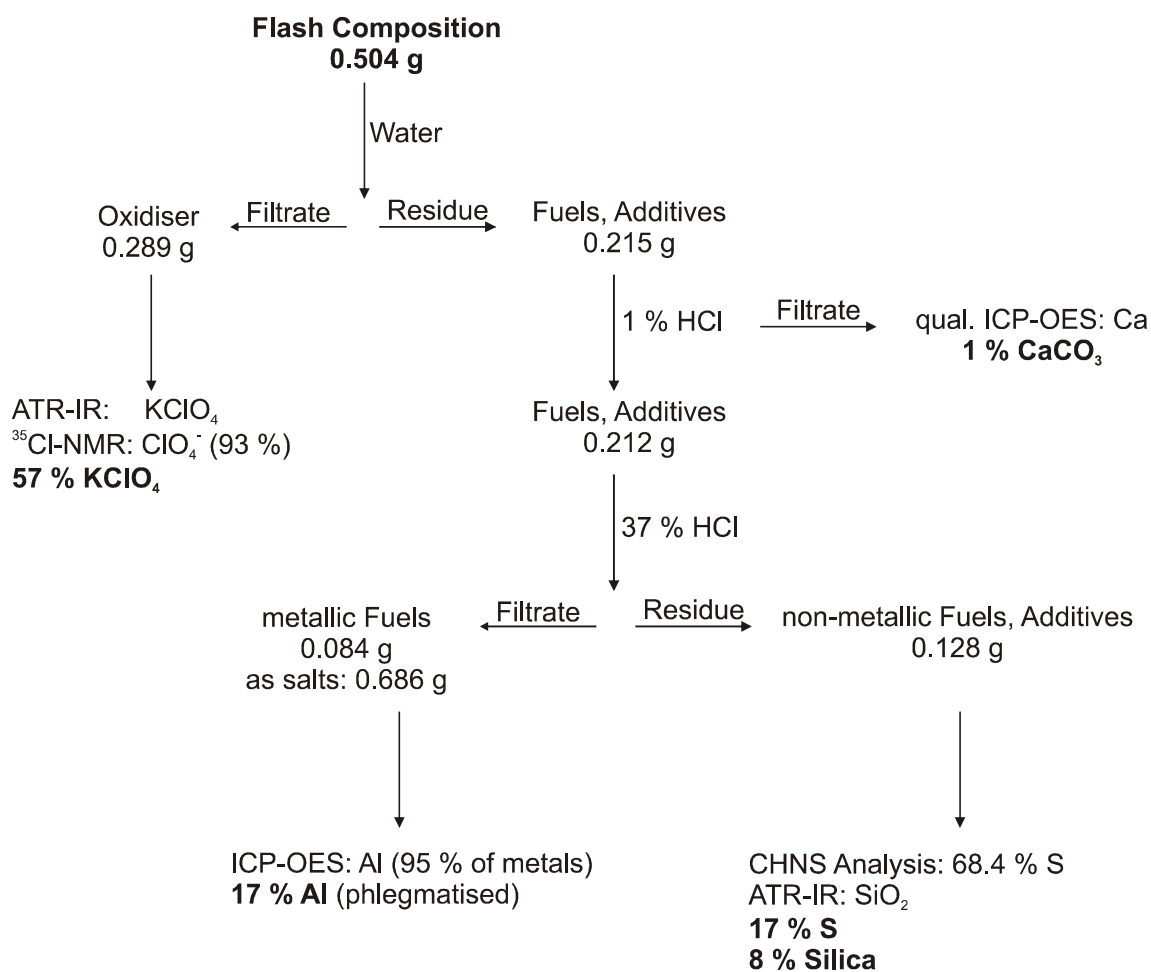


Fig. 4. Summary of the analysis of the flash composition

of the detected metals). Significant impurities are calcium, sodium and silicon. The isolated metal salt consequently can be assumed to consist of aluminium trichloride hexahydrate ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$). 0.686 g $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ equates to 0.077 g aluminium. This is nearly, but not exactly, the amount of metals which were dissolved out of the mixture (0.084 g) even if the purity of 95% is considered. Since the ICP-OES analysis cannot detect organic impurities, we assume a small fraction of the dissolved material to consist of a stabiliser for aluminium. Frequently, stearine or other oily reagents are used. Aluminium flakes are stabilised to prevent spontaneous ignition during production and storage.^{7,17} Overall, the composition contains 17% of stabilised technical grade aluminium. It should be noted that no indication of traces of titanium was found. If titanium is indicated in the ICP-OES analysis, more rigorous conditions such as mixtures of $\text{H}_2\text{O}_2/\text{HCl}$ have to be applied to completely dissolve the metal.

The slightly greyish filter residue after extraction of the metallic fuels (0.128 g) was assumed to consist

of non-metallic fuels and additives. Quantitative elemental analysis revealed an overall sulphur content of 68.4%. Consequently, the original composition contains 17% elemental sulphur. Additionally, the content of carbon and nitrogen was below the detection limit and the presence of organic fuels can be excluded.

To identify the remaining 32% of the acid insoluble

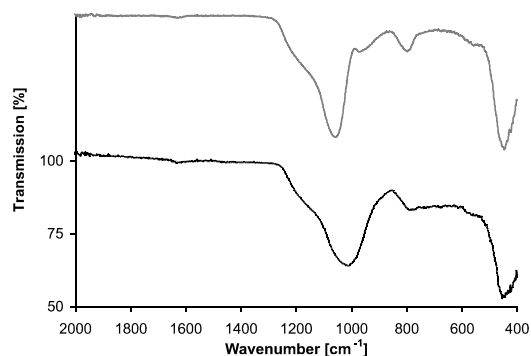


Fig. 5. ATR-IR spectra of silica (top) and the isolated acid insoluble residue (bottom).

inorganic residue, ATR-IR spectroscopy was applied. Since sulphur itself is IR inactive, a separation of the sulphur was not necessary. The spectra revealed a neat IR spectrum of silica (SiO_2) (Fig. 5). Since it was possible to obtain an IR spectrum of good quality even in the mixture containing predominantly sulphur, we assume in good conscience the last fraction (8% of the flash composition) to consist of pure silica. The large amount of silica is astonishing. Silica, usually fumed silica (Aerosil®), is a common additive for flash compositions.⁹ It is usually added to the potassium perchlorate upon mixing the flash powder to keep it free-flowing. Furthermore, the silica particles loosen and aerate the powder and consequently facilitate flame propagation. Small amounts of silica increase the strength of a flash composition.⁹ Nevertheless, 8% is an unconventionally large amount of silica. Usually, it is added in quantities of <1%.⁹ The large amount of silica is expected to act as a weak retardant. Consequently, the high silica content may explain the unconventional combustion behaviour visually between a typical flash mixture and a black powder based explosive of the pyrotechnic device discussed here. Additionally, silica may contain sodium (Na^+) bound to the huge SiO_2 surface, which may explain the yellow flame.

To estimate the constitution of the composition analysed here in comparison to well-known flash mixtures given in literature,^{7,9,17} the amount of inert silica was subtracted from the percentage composition. Thus, a relative amount of 63% KClO_4 , 18.5% Al and 18.5% S is obtained. This formulation perfectly matches not only the wider noise zone

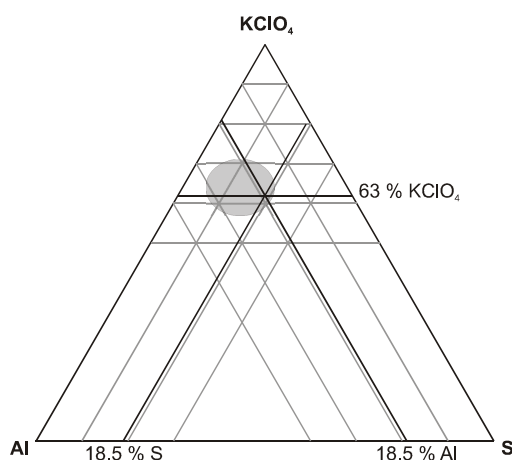


Fig. 6. Flash composition of maximal noise production (roughly indicated by the grey circle) according to Shimizu⁷ and location of the analysed flash composition (crossing of black lines) in the ternary component diagram.

for ternary flash powders containing KClO_4 , Al and S as given by Shimizu,⁷ but even the small area of optimal noise production (Fig. 6). Obviously, it has to be considered that the inert additive will reduce the power of the mixture.

Finally, it has to be noted that the knowledge about the exact chemical composition is not the full secret of a pyrotechnic mixture. The geometry of the pyrotechnic device and especially the confinement and filling level in the case of explosives based on flash powder affect the performance. Furthermore, the particle size of the chemicals is of certain interest. Obviously, generally fine aluminium flakes are used for flash.^{7,9} The influence of the particle size (in a certain range) of the aluminium on the strength of a flash mixture is generally reported to be rather small.¹⁷ Still, several studies on optimising pyrotechnic compositions by the particle size of oxidiser and fuel are present.^{20,21}

Conclusions

By the stepwise separation of the components of a flash composition into oxidisers, metallic fuels, non-metallic fuels, and additives, and subsequent analyses with state-of-the-art instrumental analytics, the full quantitative analysis of a pyrotechnic mixture is rather straightforward. The protocol reported here may readily be adapted for various other pyrotechnic compositions. The necessary analytical measurements can be provided by most chemical departments.

The full quantitative analysis of a flash composition investigated here allowed us to explain the unconventional combustion behaviour by an unexpectedly large amount of inert silica.

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