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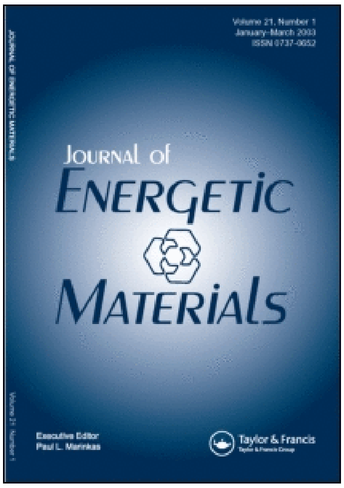

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DETERMINATION OF OXIDIZING ANIONS IN EXPLOSIVE MIXTURES BY PHASE TRANSFER

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ABSTRACT

Inorganic oxidizing agents are used in various explosive mixtures that are analysed by analytical chemists. Among them are dynamites, ANFO,black powder, match heads, pyrotechnical devices and home-made bombs. The crucial step in post explosion analysis is the extraction and purification of the explosive residues from the debris. A unique, fast and selective extraction technique for inorganic oxidizing agents is described in this paper. The debris are first extracted with water to yield an aqueous solution of the ions. Oxidizing anions such as nitrate and chlorate, are selectively transfered into the organic phase by the use of lipophilic quarternary ammonium cations. Other anions such as carbonate, sulphate and nitrite are not extracted into the organic phase under these conditions. The extracted anions are then identified by infra-red spectrometry and chemical spot tests.

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INTRODUCTION

The examination of evidence collected at scenes of explosion poses an intriguing problem to the forensic chemist.

Explosives used by terrorists and criminals alike are of three origins: military high explosives, commercial high explosives and home-made explosive mixtures. Military high explosives are usually made of organic compounds,most of the home-made explosives are based on inorganic materials and many commercial explosives are made from combinations of organic and inorganic compounds.

The isolation of organic components in pre-explosion as well as in post-explosion analyses is achieved by a varaiety of separation techniques such as column chromatography[1], thin layer chromatography[2], gas chromatography,[3,4] and high performance liquid chromatograpy.[5] Identification of the separated components is then acomplished either on-line or off-line by specific detectors[6]. Many forensic laboratories find it satisfactory to use simple chromatographic techniques in post-explosion analyses.

The methods for the identification of inorganic components of unreacted explosive mixtures include X-rays diffraction (XRD)[7], X-rays fluorescenc (XRF)[8],
infra-red spectrometry (IR)[9],ion chromatography[10] and chemical spot tests.

XRD technique is usually not sensitive enough for post-blast residues analysis, XRF is not suitable for the identification of most of the anions. Ion chromatograpy,being a chromatographic method is mainly a separation method and is not specific enough for the positive identification of the ions,IR spectrometry is not always applicable to those extracts due to interference from overlapping absorbance peaks.

In order to identify residues of inorganic oxidizing anions in post-explosion cases, it was found that a separation stage was in many instances critical. Washington et al[8] used dry sieving and microscopic examination of post-blast evidence. Other authors[7] reported using aqueous extracts followed by the aforementioned methods to greater or lesser success.

In this paper we describe the selective separation of two explosive-related anions, chlorate and nitrate by extraction based on phase-transfer. the separated anions could then be easily analysed by methods like IR spectrometry. The method is especially important in the analyses of post-explosion samples.

EXPERIMENTAL

Simulated post-explosion residues of black powder and chlorate-sugar mixtures were prepared by burning the respective explosive mixture in a crucible. Home made-explosive charges make a considerable part of the residues analysed by our laboratory hence there was no shortage of "real life" extracts at any time.

Reagents

1. Trioctylmethyl ammonium chloride (aliquat 336) from Aldrich Chemical Company Inc. Milwaukee, Wisconsin, U.S.A.

2. Tetrabutyl ammonium chloride from Aldrich

3. Methylene chloride from Frutarom, Israel.

4. Modified Greiss reagent was prepared from 8% (w/v) sulphanilamide and 0.5% (w/v) N-1-naphthylethylenediamine dihydrochloride in 8% aqueous phosphoric acid. All from B.D.H. Chemicals Ltd, Poole, England.

5. 4% aniline sulphate in concentrated sulphuric acid. From B.D.H.

Instruments

IR spectra were recorded on Analect FX 6160 FTIR spectrophotometer from Analect Instruments, Irvine, California, U .S.A.

The aqueous extract is placed in a separatory funnel, 20 mg of the tetra alkyl ammonium salt is then added and the solution is shaken once with equal volume of methylene chloride. The organic layer is separated and washed with water, dried on magnesium sulphate and finally evaporated to dryness .

If the aqueous extract from the debris is viscous , it should be extracted with methylene chloride prior to the addition of the quarternary ammonium salt. This will rid the extract from detergents and lubricant additives often found in extracts of vehicle-related explosions. The aqueous layer is then treated with the quarternary ammonium salt as described before.

RESULTS AND DISCUSSION

Inorganic oxidizing agents found in explosive devices in Israel include nitrate , chlorates and permanganates mainly as potassium salts. It is required by our standards that at least two independent methods of analysis should be used for reporting the positive identification of a substance. In the identification of residues of inorganic anions the laboratory relies on a combination of color tests and IR spetroscopy.

Nitrates are found in numerous compositions: black powder, ammonium nitrate - fuel oil (ANFO) and dynamites. failure in the identification of nitrates in post-explosion aqueous extracts may result from several reasons :

1. Greiss color reaction (for nitrates) does not discriminate between nitrite that is usually present in post-explosion extracts and the unreacted nitrate .
2. Sulphate and carbonate ions (reaction products as well as background contaminants) heavily mask the infra-red region of the nitrate absorption.

Chlorates are found in match heads and in chlorate-sugar mixtures. Sugar interferes with the IR spectrometry of chlorate in pre-explosion as well as in post-explosion analyses due to the multitude of its absorption peaks.

The separation of the anions from the aqueous solution is based on phase-transfer technique. The transfer of hydrophobic ions into lipophilic organic medium is not new. It's main application is in phase-transfer catalysis . This technique has become of increasing importance with the recognition of its potential in preparative organic chemistry. Reactions which normally proceed in aqueous media can be carried out in a binary aqueous-organic system in the presence phase transfer catalysts. Phase transfer catalysis is used in reactions such as alkylation, arylation, nucleophilic substitutions, oxidation and reduction reactions and numerous others. The special advantages of this technique are higher yields, better selectivity, shorter reaction times and milder conditions. The lipophilic character of the ion pairs is induced by the the large alkyl substituents on the nitrogen. The selectivity and the yield of a given anion transfer into the organic layer is controlled by the choice of the quarternary ammonium salt and the polarity of the organic solvent. The combination of aliquat and methylene chloride or toluene was found to be very effective in separating the oxidizing anions from the combustion products (sulphates, carbonates, chlorides, nitrites, ect.) and from background contaminants.

Sulphate, carbonate, nitrite and chloride ions remain in the aqueous layer while chlorate, nitrate and thiocyanate ions are transfered as ion pairs into the organic layer. The dried residue can now be identified by spot tests and IR spectrometry.

Burnt black powder from simulated explosion was extracted with water and dried. Spot tests applied to the extract revealed the presence of nitrites. It was not possible to distinguish by IR between the nitrite ions and the nitrate ions due to the carbonate absorbance in the relevant region (1320-1490 cm^{-1}). Aliquat extraction separated the nitrate from the nitrite and other interferring anions. Spot tests applied after the extraction were negative for nitrite and positive for nitrate. The IR spcetrum was that of aliquat nitrate . Beveridge et al reported the presence of thiocyanate in the extracts of burnt black powder and its significance as an indicator to the use of black powder as the original explosive. Aliquat extracts thiocyanate very efficiently.The thiocyanate ion can then be detected by its reaction with ferric ion and also by its characteristic infra-red bands at 1630 and 2020 cm^{-1}.

Chlorate-sugar mixtures cannot be analysed by infra-red spectrometry even before explosion because of the sugar interference. Aliquat exclusively extracts the chlorate from the aqueous solution leaving the sugar in the water and yielding a perfect infra-red spectrum of the aliquat chlorate.

In "real life" post explosion analyses it was found that in many cases, the aliquat extraction and separation step was crucial for the positive identification of the explosive used.

CONCLUSION

A novel method is described for the extraction of oxidizing anions from aqueous solutions in post- as well as pre-explosion analyses. Lipophilic quarternary ammonium cations transfer nitrate and chlorate ions into organic phases, thus freeing them from the interference of background contaminations, reaction products or other components of explosive mixtures.

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