CHROMATOGRAPHIC ANALYSIS OF EXPLOSIVES

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ABSTRACT

The applications of the column chromatographic technique for the separation, identification and estimation of the components of propellants and high explosives as well as the degradation products present in the propellants containing different stabilisers, on ageing have been reviewed.

Tswett's[1] chromatographic method of analysis has contributed very much to the progress of chemistry. Extensive use has been made of this technique for the isolation, separation, purification, detection, estimation etc. of numerous compounds. It played a fundamental role in studies in different branches of chemistry and other related fields.

This elegant technique was, however, used in the field of explosive chemistry only in recent years. In the past propellant explosives were comparatively simple mixtures consisting essentially of nitrocellulose (NC), with or without nitroglycerine (NG), and a stabiliser such as mineral jelly, carbamite (ethyl centralite or sym-diphenyl-diethyl-urea), diphenylamine (DPA) etc. Modern propellants are however, usually very complex mixtures, containing in some cases as many as ten ingredients. Further the variety of ingredients used at the present day is much greater than in the past. Consequently the products of degradation on long storage are large in number and diverse in character. The analysis of such complex propellant compositions has demonstrated very clearly the value of this method.

The first record of the chromatographic studies on the aromatic nitro-compounds appears to be that of Karrer et al[2], who described the separation and order of adsorption of ortho, meta and para nitro-anilines and the isomeric nitrophenols. The purification of the nitro-anilines and their homologues was also studied by Karrer et al[2] and Kuhn et al[3]. Shinomiya[4] studied the behaviour of di-and tri-nitro-toluenes and similar compounds on columns of alumina.

Halftar[5] was the first to describe the technique exclusively for explosives. This author carried out a separation of dinitro-toluene (DNT) and trinitro-toluene (TNT) using columns of magnesia mixed with calcium hydroxide. Mitra and Srinivasan[6] investigated the behaviour of some high explosives and also the effect of sunlight on tetryl. Talc or Kaolin was used by these authors as the adsorbent except with mono-nitro-toluene (MNT), which was dissolved in toluene and passed through an anhydrous sodium carbonate column.

During the years 1943—47, column chromatography was employed in a number of investigations by Ovenston[7,8,9] and Parker[10] at the Naval Ordnance Inspection Laboratory in Dorset, England and by Schroeder et al[11,12,13] at the California Institute of Technology, U.S.A. Both schools of investigators were constantly in touch with each other through official channels.

These investigations were concerned with the examination of high explosives and propellants. Analysis of new propellant compositions captured during World War II, and studies of the products formed and the reaction mechanisms involved during the ageing of propellants with different stabilisers, viz. carbamite, acardite (AC or 1 : 1-diphenyl urea), carbazole (CBZ) and triphenylamine (TPA) constituted the principal contributions. Attempts were made to correlate the analytical data on the products formed with the thermal age (ballistic propertie and useful service life) with partial success.

The salient points of the technique adopted by the above authors are given below :

Absorbents

Silica gel was found to be the best adsorbent in all cases, except mineral jelly. A fine commercial grade of it was selected and since filtration through such a bed was slow, it was mixed (1 : 1) with celite-535 which served as a filter aid. This mixture was found to be by far the most useful and satisfactory chromatographic adsorbent for handling explosives and related compounds. Experimental details for the most satisfactory method of packing the adsorbent in the tube are given by Ovenston[9].

Activated alumina was used as adsorbent for mineral jelly by Ovenston[7] and for the quantitative separation of DPA, 1-nitro-naphthalene and naphthyl methyl ether by the same author[8]. It was, however, found to be of limited use[9] for the following reasons:—(*a*) recovery by elution was more nearly quantitative with the silica gel than with alumina; (*b*) polynitro-aromatic compounds could be satisfactorily chromatographed on silica gel while activated alumina was useless for the purpose; (*c*) many compounds of interest (e.g. nitro-substituted mono—and di-alkyl anilines) were found to undergo complex transformation reactions in contact with activated alumina; no such change took place with silica gel; (*d*) when acetone was used as a developing solvent, diacetone alcohol and mesityl oxide were formed in appreciable quantities on an alumina column and this modified the developing power of the solvent. Silica gel did not have this defect, and finally (*e*) silica gel is comparatively inexpensive and may be readily recovered and re-activated, without apparent alteration in properties.

Of the other adsorbents tried[9], most of the silicates, including fuller's earth and kaolin, tended to bring about decomposition of many amino-aromatic compounds of interest. None of them appeared to have any advantage over silica gel. Calcium hydroxide and magnesium oxide were used in some cases for qualitative work since enhanced colours were given by these alkaline adsorbents to nitro-aromatic compounds. This fact was exploited by Halfter[5], but Ovenston[9] found that the zones were too irregular and diffuse for quantitative work.

Solvents

In his investigations on the ageing of cordite SC, Parker[10] extracted the sample with ether. The dried residue from this extract was dissolved in a mixture of benzene and light petroleum and chromatographed. The chromatogram was developed with ethyl ether and petroleum mixture. The different portion of the chromatogram were eluted with alcohol.

Ovenston[9] used a mixture of acetone in light petroleum as solvent for nitro-aromatic solids, mostly high explosives. The chromatogram was developed with benzene in light petroleum. For the propellant ingredients, a mixture of ethyl ether in light petroleum was employed as the solvent. Benzene in light petroleum served as the developer.

In the scheme for the detection of ether soluble propellant ingredients, Ovenston[8] dissolved the residue from the ether extract in a suitable developing solvent and then used the solution for chromatography. The components and the percentage composition of the developing solvent varied with the ingredients under investigation.

Schroeder et al[11] extracted the test samples of aged propellants with methylene chloride. NC remained undissolved. Developing was done with acetone-ligroin, ether-ligroin or benzene-ligroin in different cases.

Ovenston[7] extracted a mineral jelly cordite with ether and dissolved the residue, obtained by evaporating the ether, in light petroleum. The mineral jelly was partially adsorbed by the column of alumina.

Methods

The chromatographic behaviour of selected nitroso-amines was established by Parker[10]. From measurements of a large number of chromatograms of pairs and groups of compounds on silica gel-celite adsorbent, Ovenston[9] compiled tables showing orders of adsorption using various developing solvents. These tables proved to be of considerable assistance in devising schemes for the separation of components of mixtures. The nitro-aromatic solids, mostly high explosives formed one class and the ether-soluble propellant ingredients another. A scheme for the chromatographic detection of any of twenty four possible ether soluble propellant ingredients in presence of one another was developed by Ovenston[8]. Once the qualitative composition was known, chromatographic and conventional methods could be used for quantitative analysis of any group of ingredients.

Of the many ingenious methods for locating zones of colourless compounds, the "streak" technique of Zechmeister et al[14] was widely used in the chromatographic analysis of explosives by Parker[10], and Ovenston[9]. The following reagents were used: (*a*) Sodium hydroxide (6N); (*b*) diphenylamine dissolved in sulphuric acid. (*c*) an acid solution of potassium dichromate, (*d*) sulphuric acid, concentrated, and (*e*) bromocresol green solution. When it is desired to follow the course of the development of a chromatogram of colourless compounds, however, these streak tests are inapplicable.

Brockmann[15] developed a method of using internal indicators for distinguishing the zones of the colourless substances on the adsorbent column. In this method a small quantity of one or more coloured compounds is added to the original solution before chromatography. The relative rates of development of the indicator and the compound sought are known from previous experiments, and the indicator zone serves to locate the compound so that development may be stopped at the desired point and the extruded column can be cut at the appropriate place without contaminating the zone with streak

reagents. This technique was adopted by Parker[10] in the course of his investigations on the ageing of cordite SC and by Ovenston[7,9] in his investigations on propellant explosives.

Illumination of the column with U.V. light was not of much help since the great majority of the explosive components of interest did not fluoresce[9]. Recently, however, fluorescing columns were employed to observe zones of colourless compounds by the "shadows" they produced. The adsorbents used were either treated with a fluorescent organic compound such as morin (Brockmann and Volpers[16]) or admixed with a small proportion of fluorescent zinc sulphide (Sease[17]). Silica gel treated with "Belloid TD" (a sulphonated condensation product of naphthalene and formaldehyde), was used by Ovenston[9] and was found to be of great value in the chromatography of explosives and related materials. The shadow cast by a zone containing one milligram of TNT, for instance, could be seen. The separation of similar quantities of ortho and paranitro-toluenes, for which no simple streak test was found, could be similarly followed. By using a developer consisting of 10% benzene in light petroleum, two separate "shadows" could be developed, showing the normal bright fluorescene between them.

When the presence of a compound was indicated by a streak test, a sufficient quantity of it was separated by elution and confirmatory tests carried out. The large number of existing colour. "Spot Tests" were useful in this respect. Determination of refractive index was of help in the identification of nitric esters. In case of doubt, a mixture of the "test sample" and an authentic sample with which it was believed to be identical was chromatographed. The development of a single zone confirmed identity.

Most of the new ingredients were best identified by their U.V. absorption spectra, which could readily be obtained on an alcoholic eluate and compared with standards. The speetro-photometer was used to determine the propellant ingredients by Schroeder[18].

Applications

(1) The main advantage of the chromatographic technique in the analysis of high explosives—the nitro-aromatic compounds such as MNT, DNT, TNT etc. lies in the very small quantity of the sample which is required. Common explosives such as hexa-nitro-DPA, tri-nitrophenylmethyl nitramine and TNT were very readily separated quantitatively. The method was applied to the examination of mixtures. and also proved useful in examining small quantities of TNT for suspected contamination with trinitrophenyl methyl nitramine. (Ovenston[9]).

(2) Ovenston[7] developed a method for the identification and estimation of mineral jelly in propellants on an alumina column. The method depends on the wide differences between the chromatographic adsorption characteristics of mineral jelly and those of other ether-soluble propellant ingredients.

(3) During the normal life of cordite SC in which carbamite is the stabiliser, N-nitroso-N-ethylaniline and its 4-nitro-derivative are formed in noticeable amounts (Lecorche and Jovinet[19]). After prolonged periods of accelerateld ageing, however, very small amounts of the 2-nitro, 3-nitro-, 2 : 4-di-nitro-, and

2 : 4 : 6-trinitro-derivatives of N-nitroso-N-ethyl-aniline are formed. These compounds were isolated and identified by the chromatographic method. (Ovenston and Parker[20], and Parker[10]).

Lecorche and Jovinet[19] suggested that an indication of the thermal age of the propellant could be obtained by determining the "Total Nitroso-amine" content by means of the colour reaction (blue-violet) of the nitroso-amine and α-naphthylamine hydrochloride. This colour reaction was fully studied by Parker[21] and later applied by Ovenston and Parker[20] for the accurate determination of the "Total Nitroso-amine" content. A "Spekker" Photo-electric absorptiometer with Ilford yellow-green filter No. 605, was used and a calibration graph obtained with known amounts of pure N-nitroso-N-ethylaniline.

The percentage "Total Nitroso-amine" content was plotted against the thermal age of a large number of samples of cordite SC which had been stored at the normal service "Climatic Trial" temperature of 49°C (120°F). The points occupied a fairly narrow zone on the graph, and the individual points could be produced almost exactly in duplicate determinations indicating that the variations among the equally aged samples were due to slight differences in stability of the lots manufactured at about the same time. Using this graph, the equivalent thermal age of any given sample of cordite SC could be determined. This method possessed advantages over the older methods viz., (*i*) Colour Number, and (*ii*) Fall in Stabiliser Value. It was not an empirical method and could be adapted to far smaller quantities of propellant than can be examined by other available methods. Further, compatibility of other materials with cordite could be assessed more accurately by this method than the "Fall in Stabiliser Value" method.

In order to estimate the individual nitroso-amines, a chromatographic method of separation was developed by Parker[10]. The individual components could then be estimated colorimetrically. The results obtained served to clarify the mechanism of the transformation of the stabiliser. This procedure enabled a study to be made regarding the effect of various factors upon the distribution of the transformation products. The relative proportions of N-nitroso-N-ethylaniline and its 4-nitro-derivative gave some indication of the previous thermal history of the cordite. (Parker[10]).

Visual examination of the chromatogram enabled a distinction to be drawn between a cordite which had developed a high "Heat Test" through storage in a hot magazine and another which had developed a similar condition through exposure to sunlight (Ovenston[9]).

(4) During the World War II many strange propellant composition from foreign sources were examined successfully by Ovenston et. al[9]. The accurate analysis of these compositions was only possible through chromatography.

(5) Chromatography was applied to the investigation of causes for certain colourations in cordite. The yellow and pink colours on newly manufactured batches of cordite were shown to be due to 4-nitro-N : N^1-diethylaniline and an azo dye respectively. The former was considered to be formed during manufacture from small quantities of diethylaniline present as an impurity in one of the normal ingredients, carbamite. The latter was traced to the presence

of a little primary amine together with diethylaniline. The slow, incipient breakdown of the nitric esters produced enough nitrous acid to yield azo dyes (Ovenston[9]).

(6) The extreme usefulness of the chromatographic technique is well illustrated by the separation of carbamite from methyl centralite, which occur together in propellant compositions (Ovenston[9]).

(7) DNT and DPA which are present together in modern NC powders could be readily identified by appropriate streak tests on the chromatogram (Ovenston[9]).

(8) The products formed on accelerated ageing of propellants stabilised by DPA were investigated using chromatography by Schroeder et al.[11] A large number of derivatives of DPA were isolated and characterised. Reaction mechanisms were suggested. These studies provide methods by which it was possible to determine roughly quantitatively the state of DPA originally incorporated as stabiliser. However, it was found that several points needed clarification before any satisfactory relationship could be established between the condition of the powder (ballistic usefulness or safe life) and the state of the stabiliser, as represented by analytical data.

(9) Schroeder et al[12] also studied the products formed during accelerated ageing of propellants stabilised by carbamite using the above technique. One Solventless Process Cordite, JP 76, which originally contained 9% of carbamite in addition to NC and NG, and one Solvent Process cordite, RPL 142, which contained only 1% of carbamite were examined. From the two samples, as many as forty compounds were isolated and about half of them identified. Reaction mechanisms were suggested. These authors concluded that the ballistic usefulness and the safe life of a powder could not be determined from a knowledge of the state of the stabiliser.

The rates of depletion of carbamite and DPA were compared. It was however, concluded that it was inadvisable to draw conclusions about the merits of different stabilisers from studies on the rate of depletion of a stabiliser. Rapid depletion of one does not necessarily mean that the stabiliser was less efficient than the other; on the other hand, it might mean that it was more effective in combining with the deleterious products in the powder and the other inert. Further, effectiveness not only depended on the original stabiliser itself but also on that of the derivatives.

(10) Schroeder et al[13] employed chromatography to investigate the products formed during accelerated ageing of double base powders stabilised by acardite (AC), carbazole (CBZ), and triphenylamine (TPA). These authors found that AC gave only derivatives of DPA and no nitro-acardites could be isolated. CBZ behaved similarly to DPA.

TPA was found to differ very greatly in its reactions from the other stabilisers. Its reactions followed clear cut and definite stages in which each compound was converted into one main precursor only. Reaction mechanisms were suggested in all the three cases. The rates of depletion of the different stabilisers were determined using the same technique. TPA was exhausted more slowly than DPA but more rapidly than AC, CBZ or carbamite. The latter three were

depleted during the same period of time, although the reactions were different in the three cases.

Conclusion

The practical utility of the chromatographic technique in investigations dealing with compositon, stabilisation and thermal age of propellants, and the composition of high explosives is well illustrated by the examples mentioned above. The technique does not need any elaborate or expensive equipment and is consequently highly suited to routine work. Although it is a time-consuming method, it is a valuable tool in the examination of complex problems where other direct methods are not available. If the components of a mixture could be estimated directly by standard methods, there is no particular advantage in using chromatographic methods. However, the analysis of the more complex mixtures will be greatly assisted by the use of chromatographic separations.

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