

## PAPER CHROMATOGRAPHY OF NITRO COMPOUNDS

## I. SUBSTITUTED TRINITROBENZENES\*

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## INTRODUCTION

Preliminary investigations demonstrated that paper chromatography would be the most efficacious method for determining the purity of some explosives that were under investigation in this laboratory. With the exception of the excellent work by ETTTEL, POSPILSIL AND DEYL<sup>1</sup> there is very little information dealing with the chromatography of polynitro aromatic compounds. The author hopes that this report will help to fill the hiatus in this subject.

## APPARATUS AND REAGENTS

An all glass apparatus\*\* was designed to eliminate the many objections found with the conventional stainless steel and glass apparatus.

Whatman No. 1 chromatographic grade paper.

One microliter (1  $\mu$ ) self filling pipets.

All chemicals were of reagent grade if obtainable, or else they were purified by appropriate means.

The laboratory, where the chromatographic runs were carried out, was maintained at  $23^{\circ} \pm 0.5^{\circ}$  and the relative humidity was kept in the range of 42-45 %.

## EXPERIMENTAL

This investigation is limited to partition studies using formamide or heavy mineral oil to impregnate Whatman No. 1 paper. Unless specifically stated, the paper was not washed either before or after impregnation. All chromatograms were made using the descending technique.

The paper was cut into strips 37 cm  $\times$  10.4 cm, with the length following the machine direction. Lightly pencilled lines were drawn at 4 cm, 9 cm, and 34 cm from one end. The strip was divided into 1.9 cm intervals on the 9-cm line, thus allowing 5 compounds to be run simultaneously. All chromatograms were allowed to descend for 25 cm. The approximate times for each solvent system are given in Table I.

\* This work was performed under the auspices of the U.S. Atomic Energy Commission.

\*\* Commercially available from Kensington Scientific Corporation, 1717 Fifth Street, Berkeley, Calif., U.S.A.

A 25% solution of formamide in acetone was used for the polar phase studies and a 10% solution of Squibbs heavy mineral oil in *n*-hexane was used for the reversed phase experiments. The strips were drawn through the impregnating solutions with a steady motion and hung to dry in the laboratory. Drying time before spotting is 15 minutes for the formamide papers and 5 minutes for the mineral oil papers.

One microliter (1  $\lambda$ ) of a 1% (w/v) solution, of the particular compound dissolved in acetone, was spotted for each run. In the case of 2,4,6-trinitro-1,3-diaminobenzene, two 1  $\lambda$  aliquots of a saturated solution in acetone were spotted on the paper.

The systems chosen progress from low dielectric to high dielectric solvents and finally to ionizing polar solvents. Table I lists the partition systems that were used in this study of fourteen substituted trinitrobenzene compounds. The papers were conditioned 30 minutes in the closed chromatographic tank before adding 10 ml of the mobile phase.

TABLE I  
PARTITION SYSTEMS

Number	Stationary phase	Mobile phase	Approximate time to travel 25 cm
1	Formamide	<i>n</i> -Hexane	1 h
2	Formamide	Carbon tetrachloride	2 h 30 min
3	Formamide	Benzene	2 h
4	Formamide	Benzene-ethyl acetate (1:1)	2 h 15 min
5	Mineral oil	Methanol-ethyl acetate (1:1)	4 h
6	Mineral oil	Methanol-3-pentanone (1:1)	3 h 30 min
7	Mineral oil	Methanol-water (3:1)	6 h
8	Mineral oil	Water	2 h
9	Mineral oil	0.1 <i>M</i> Ammonia	2 h
10	Mineral oil	0.1 <i>M</i> Hydrochloric acid	2 h

Except for 1,3,5-trinitrobenzene, 2,4,6-trinitrobenzoic acid, and tetryl, the remaining compounds are self indicating. The exceptions are easily identified when the chromatogram is viewed by short-wave ultraviolet light. No other detection methods were used.

#### DISCUSSION AND RESULTS

The  $R_F$  data are presented in graphical form, giving a profile or "chromatographic spectrum" of a compound in the ten systems that were studied (Figs. 1-7). An additional point of interest has been added that is not usually given with  $R_F$  data; *i.e.*, the length of the spot. LACOURT *et al.*<sup>2</sup> have advocated the use of the double  $R_F$  notation, which the author has found to be very useful when describing the appearance of a chromatographic spot. This is illustrated in the graphical presentation of the data. The vertical line shown for a compound in the particular system denotes the length of the chromatographic spot. Knowing the front and rear  $R_F$  values, makes the selection of the best partition system for separating two or more compounds easier.

All compounds that contain a phenolic group had zero  $R_F$  in the systems containing formamide as the stationary phase. This could be due to a strong hydrogen bonding between the hydroxyl group and the formamide. Neither the amino nor the methyl group, *e.g.*, in 2,4,6-trinitro-3-aminophenol or 2,4,6-trinitro-*m*-cresol had

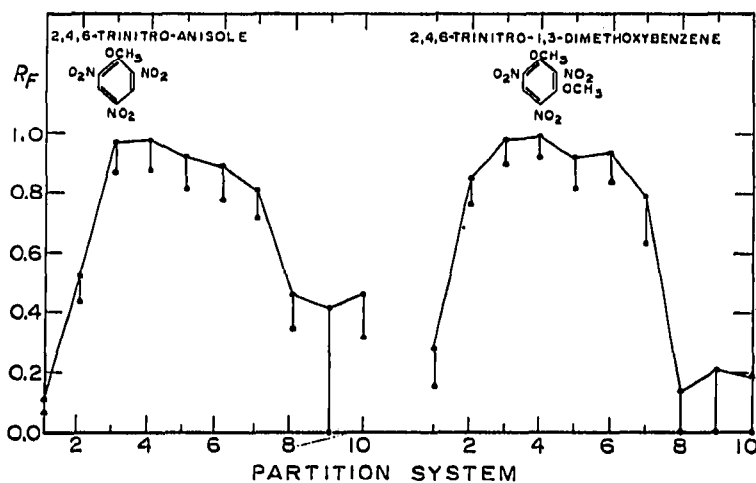


Fig. 1.  $R_F$  values of 2,4,6-trinitro-anisole and 2,4,6-trinitro-1,3-dimethoxybenzene.

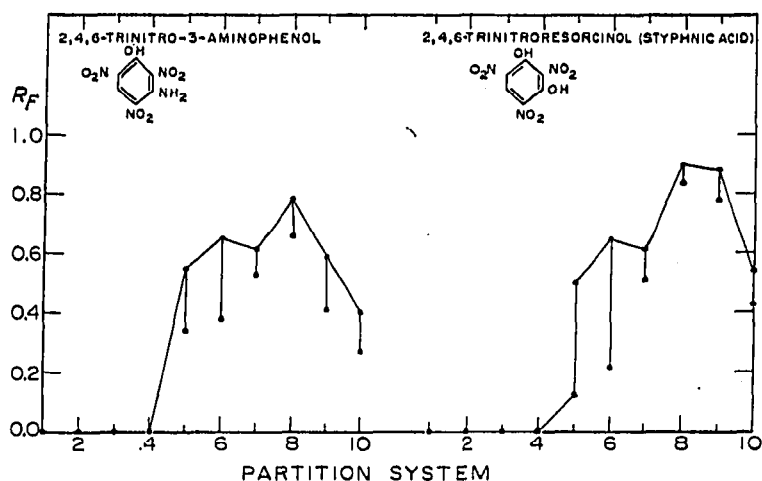


Fig. 2.  $R_F$  values of 2,4,6-trinitro-3-aminophenol and 2,4,6-trinitroresorcinol (styphnic acid).

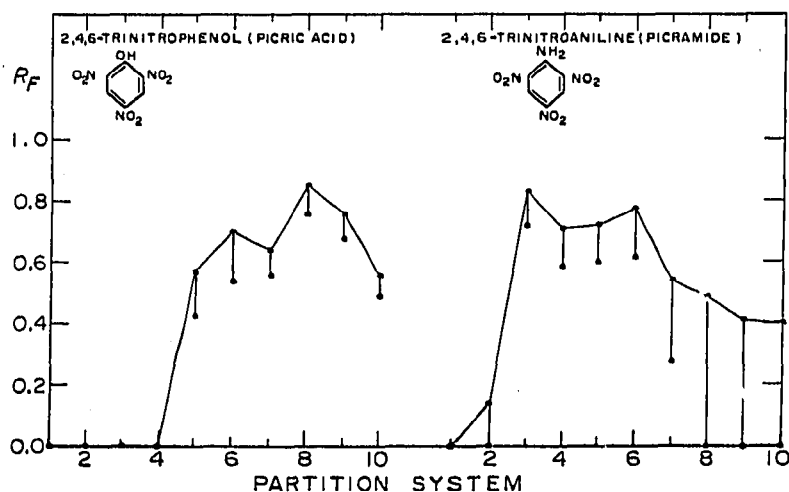


Fig. 3  $R_F$  values of 2,4,6-trinitrophenol (picric acid) and 2,4,6-trinitroaniline (picramide).

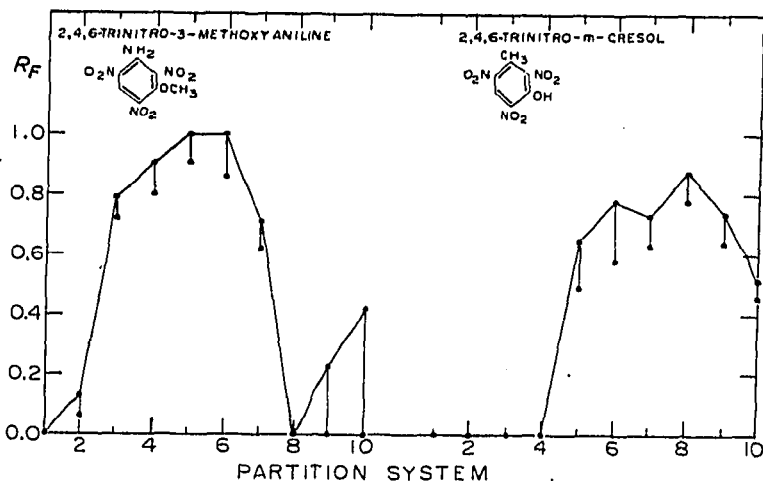


Fig. 4.  $R_F$  values of 2,4,6-trinitro-3-methoxyaniline and 2,4,6-trinitro-*m*-cresol.

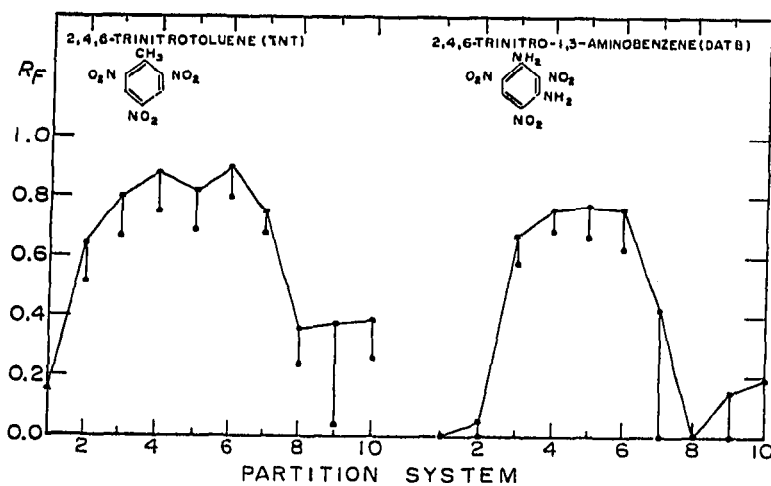


Fig. 5.  $R_F$  values of 2,4,6-trinitrotoluene (TNT) and 2,4,6-trinitro-1,3-aminobenzene (DAT B).

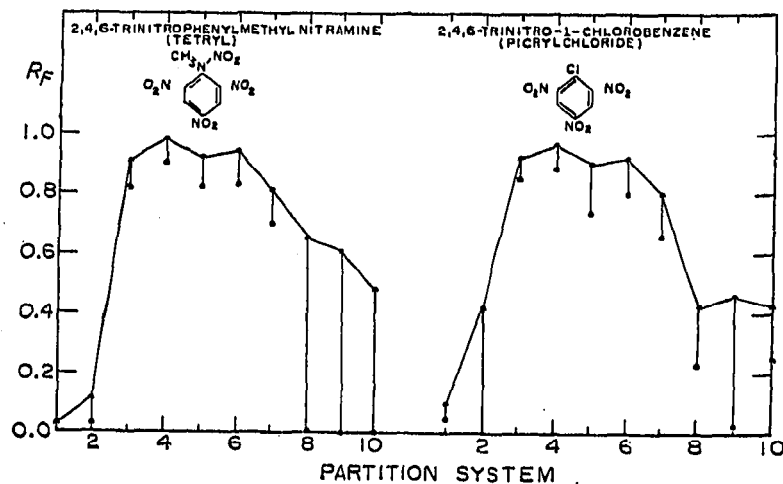


Fig. 6.  $R_F$  values of 2,4,6-trinitrophenyl-methyl-nitramine and 2,4,6-trinitro-1-chlorobenzene (picryl chloride).

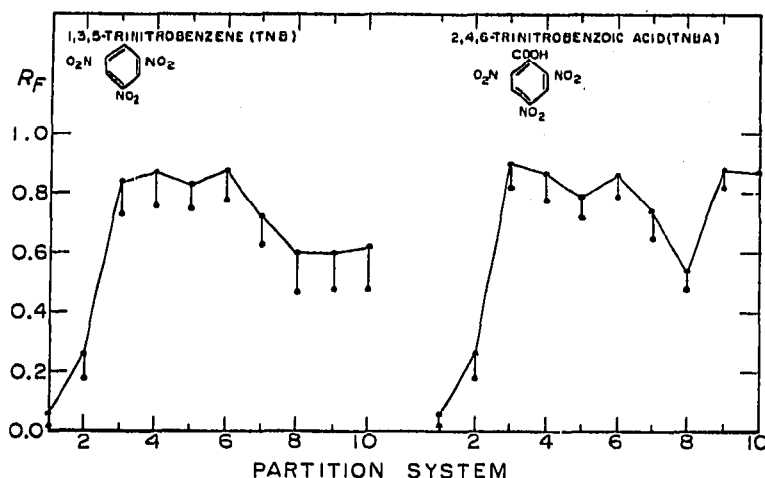


Fig. 7.  $R_F$  values of 1,3,5-trinitrobenzene (TNB) and 2,3,6-trinitrobenzoic acid (TNBA).

any effect in changing the  $R_F$ . Therefore, one has a fairly rapid method of separating phenolic-containing compounds from the others.

In general, substances containing the amino, methoxy, and chloro groups tailed very strongly or did not move in systems 8, 9, and 10, whereas the hydroxy compounds moved nicely. As yet no valid explanation has been found for this behavior.

From the data, it appears from a chromatographic viewpoint that there is not much difference between the effect of a methoxy or chloro substitution on the  $R_F$  value. And, in the systems studied, a separation of 2,4,6-trinitro-anisole from picryl chloride was not achieved. Whether the analogy between the methoxy group and the chloro group can be applied to the remaining halogens is not known as yet.

The most noteworthy point that deserves mentioning is that water alone is a valuable chromatographing solvent for this class of compounds. The majority of substances moved and gave well defined spots.

A preliminary study of the principles set forth by BATE-SMITH AND WESTALL<sup>3</sup> and FRANC AND LATINAK<sup>4</sup> indicates that the probability of predicting structure and  $R_F$  of various trinitro-aromatic compounds is quite good. This subject will be expanded into a future publication.

#### SUMMARY

Fourteen substituted trinitrobenzene compounds have been chromatographed in ten partition systems. The data, when presented in graphical form, gives one a profile or "chromatographic spectrum" of a particular substance. This method simplifies the choosing of a proper solvent system to achieve the best separation of compounds in a mixture.

#### REFERENCES

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