

## Metallic nitrates in paper chromatography

### VI. Systems containing tri-*n*-butyl phosphate and nitric acid\*

Continuing our studies<sup>1-5</sup> on the chromatographic behaviour of metallic nitrates in those organic solvents that are used for extraction in radiochemistry, we have recently investigated the usefulness of tri-*n*-butyl phosphate (TBP) as an eluant in partition chromatography.

TBP has undoubtedly become one of the most favoured organic solvents for the separation of fissile and fertile materials. The extraction of the actinides and rare earths by TBP and the conditions for the separation of these elements from one another have been extensively studied<sup>6</sup>. A chromatographic separation of nickel from cobalt by TBP in hydrochloric acid media has recently been reported<sup>7</sup>.

Since partition chromatography provides results that are related to the distribution coefficients obtained by the extraction technique, we investigated the chromatographic behaviour of the 59 cations (with the exception of osmium) and anions listed in the preceding paper<sup>5</sup>. In addition to the ions known to form complex species that can be extracted from nitric acid solutions by TBP, it was found that the following ions moved on the paper with appreciable  $R_F$  values: calcium, magnesium, aluminium, beryllium, indium, manganese, selenium, rhenium, iron, molybdenum, vanadium, technetium, bismuth, zinc and iodine. Furthermore, the covalent chloride compounds of antimony, tin and palladium were appreciably extracted by TBP.

During the first preliminary experiments, several technical difficulties were encountered. The TBP solvent continued to move along with the spots on the paper even after the run of the chromatograms had ceased, which necessitated an immediate developing of the chromatograms. Further difficulties arose in the developing of the spots, owing to the stable metallic complexes formed with the TBP. The most serious disadvantage was the tailing of the spots on the paper. In order to overcome the difficulties encountered, nearly all the factors that influence the chromatographic behaviour of ions were investigated. Experiments were carried out varying: (1) the technique employed, (2) the initial concentration of nitric acid and/or of inorganic nitrates, (3) the organic diluents and (4) the concentration of TBP in the organic diluent.

Both the ascending and descending techniques were employed. By using longer sheets of paper in the descending technique we succeeded in shortening the tailing appreciably and in obtaining well defined spots. Some experiments were carried out using paper impregnated with TBP. Only a very slight migration of the ions ( $R_F \leq 0.1$ ) occurred on these papers, independent of the nitric acid concentration.

Whatman papers Nos. 1, 2, 3 and 4 were compared, using the radioactive tracer

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technique. In this way the difficulties encountered in the developing of the chromatograms were eliminated. Whatman No. 4 was found to be the most suitable in most cases, since it gave well defined spots.

The  $R_F$  values of most of the ions are not influenced when the nitric acid concentration is varied between 1 and 16  $M$ , although for some cations a minimum concentration of the acid is necessary to obtain  $R_F$  values other than zero. The type of nitrate (lithium, sodium or ammonium nitrate) in the aqueous solution also had no marked influence on the  $R_F$  values measured.

In practice TBP is diluted with an inert solvent, usually kerosene. Our experiments were carried out with 0 %, 5 %, 20 % and 50 % TBP, and also with 100 % TBP; di- and mono-butyl phosphate had previously been removed from the TBP<sup>8</sup>. In solutions containing 0 % and 5 % TBP, all the ions investigated had  $R_F$  values equal to zero. An increase of the TBP content from 20 % to 100 % caused only a slight increase in the  $R_F$  values. With 100 % TBP the tailing of the ions was less in several cases; when the descending technique was employed quite well defined spots were obtained.

Purified and redistilled odourless kerosene boiling between 210°–250° was used in most of the experiments. Instead of kerosene, carbon tetrachloride, chloroform, heptane, toluene, petroleum ether, butanol and methyl isobutyl ketone were also tried. None of these solvents showed any great advantages over kerosene. When butanol or methyl isobutyl ketone were used as diluents, double-spots appeared in several cases, probably due to the diluents themselves being capable of extracting the ions.

Summarizing, it can be said that the number of ions that migrate on the paper is significantly larger than the number that up till now have been reported to be extractable from aqueous nitric acid solutions by TBP. Neither the amount of TBP in the diluent, nor the nitric acid concentration of the aqueous phase had an appreciable influence upon the  $R_F$  values obtained. This is in contrast to what was observed in the case of the extraction technique.

A more detailed report, including numerical data for the ions investigated, will be published in due course.

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