

# METALLIC NITRATES IN THE METHYL ISOBUTYL KETONE-NITRIC ACID SYSTEM

## A PAPER CHROMATOGRAPHIC STUDY

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In radiochemical separation processes the chief object is often the efficient extraction of relatively small concentrations of elements formed in irradiation fuels. The starting materials are usually solutions of the fuel in nitric acid of varying concentrations. The selection of a solvent for carrying out a given separation involves a number of considerations<sup>1</sup>. The organic extractants at present most favoured and most widely employed for these separations are methyl isobutyl ketone (MIBK) also called hexone and tributyl phosphate<sup>2</sup>.

Since essentially the same information may be obtained from the determination of distribution coefficient and  $R_F$  values, the technique of paper chromatography has been applied to the field of radiochemical investigations. For this purpose it is important to know the  $R_F$  values of as many ions as possible in one given solvent system. A considerable amount of chromatographic work along these lines has been done on metallic complexes, but most of the work appears to have been restricted to halides<sup>3, 4</sup> and—in common with most work in this field—butanol was chosen as the solvent. In the literature there are only isolated reports of experiments in which nitric acid was used in paper chromatographic studies. In spite of the promising results obtained with this solvent using the extraction technique<sup>1, 2, 7</sup>, no work has so far been published on MIBK as an eluting solvent in paper chromatography.

In this study a comparison was made of the chromatographic behaviour of various metals in the MIBK-nitric acid system. Some of the properties of MIBK as a solvent in the presence of various concentrations of aqueous nitric acid are reported.

### EXPERIMENTAL

Methyl isobutyl ketone was a Shell pure commercial product and was distilled before use. "Baker's Analyzed" nitric acid, sp. gr. 1.422, was employed.

0.5, 1, 2, 3, 4, 5, 6 and 8 *M* aqueous nitric acid solutions were prepared by taking aliquots of a 10 *M* nitric acid stock solution. 150 ml of the aqueous solutions of nitric acid (freshly diluted from the freshly prepared 10 *M* acid) was mixed with equal volumes of MIBK in a glass-stoppered bottle and equilibrated by mechanical

shaking at room temperature ( $25^\circ \pm 2^\circ$ ) for 15 min. The bottle was removed from the shaker, the contents transferred to a separatory funnel, 10 min time allowed for separation, and the phases separated. The nitric acid distribution was determined from 10–25 ml aliquots of both layers, taken by pipetting. The portions were transferred to volumetric flasks. The aqueous layer was diluted with water, the MIBK layer with ethanol. The concentrations of nitric acid were determined titrimetrically using a Beckman Model H2 pH meter equipped with glass and calomel electrodes, which were checked against a standard aqueous buffer solution. The aqueous solutions were titrated with aqueous sodium hydroxide, and the organic phases with ethanolic sodium hydroxide, the latter being frequently checked against aqueous hydrochloric acid.

The experimental chromatographic technique, the reagents and methods for detection of spots have been described in a previous paper<sup>3</sup>. The chromatograms were developed at room temperature for 2–6 hours, depending on the acid concentration.

## RESULTS

### *Distribution of nitric acid*

Table I shows the calculated distribution coefficients. In all cases the total amount of nitric acid found, differed from the amount originally in the aqueous nitric acid

TABLE I  
DISTRIBUTION OF NITRIC ACID BETWEEN WATER AND METHYL ISOBUTYL KETONE

$M[\text{HNO}_3]$ in original aqu. layer	$\frac{[\text{HNO}_3]_o}{[\text{HNO}_3]_w}$
0.5	0.076
1	0.112
2	0.221
3	0.290
4	0.350
5	0.394
6	0.437
8	0.480
10	0.518

solution added, by at most  $\pm 1\%$ . The coefficients found differ somewhat from those obtained by Koor<sup>5</sup>. His results are somewhat higher, showing a greater solubility of nitric acid in the organic phase, especially at higher acid concentrations. These discrepancies are explicable on the assumption that the nitrogen oxide vapours that develop over more concentrated aqueous nitric acid solutions on standing are soluble in the organic phase. In our experiments the two liquids were mixed and equilibrated immediately after preparing the 10 *M* stock solution of nitric acid and its dilution, so that the possibility of nitrogen oxides leaving the aqueous solution was avoided.

### Stability of MIBK-nitric acid solutions

CULLER<sup>2</sup> pointed out the possibility of reaction of MIBK with concentrated nitric acid. We originally planned to extend our study to higher nitric acid concentration than 10 *M*. Under our working conditions it was, however, impossible to mix 12 *M* or more concentrated aqueous nitric acid solution with MIBK. On mixing the two liquids a vigorous reaction took place after a few minutes. The ketone was oxidized to butyric acid (recognized by its unpleasant odour) and nitrogen oxides were liberated.

The separated MIBK layer saturated with 10 *M* aqueous nitric acid undergoes a similar reaction. The time necessary for the oxidation of the ketone is probably dependent on the amount of nitrogen oxide vapours above the aqueous nitric acid solution previous to mixing with the ketone. Thus, fresh 10 *M* solution prepared from non-fuming nitric acid decomposes MIBK only after 24 hours. The same aqueous nitric acid solution mixed with MIBK after a week, oxidizes the MIBK within a few hours. MIBK saturated with freshly prepared 8 *M* aqueous nitric acid decomposes after a week, while when saturated with the same nitric acid solution a week after its preparation it decomposes during the first night; saturated with a fresh 6 *M* solution it only oxidizes after four weeks.

### Paper chromatographic experiments

The  $R_F$  values of most of the ions investigated were equal to zero independent of the concentration of nitric acid.

The fission product elements were spotted on filter paper as:

Th(NO <sub>3</sub> ) <sub>4</sub>	UO <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	Ce(NO <sub>3</sub> ) <sub>3</sub>	Ce(NO <sub>3</sub> ) <sub>4</sub>	Zn(NO <sub>3</sub> ) <sub>2</sub>
Sr(NO <sub>3</sub> ) <sub>2</sub>	AgNO <sub>3</sub>	In(NO <sub>3</sub> ) <sub>3</sub>	Ba(NO <sub>3</sub> ) <sub>2</sub>	La(NO <sub>3</sub> ) <sub>3</sub>
Sn(NO <sub>3</sub> ) <sub>2</sub>	Y(NO <sub>3</sub> ) <sub>3</sub>	ZrO(NO <sub>3</sub> ) <sub>2</sub>	Cd(NO <sub>3</sub> ) <sub>2</sub>	Sm(NO <sub>3</sub> ) <sub>3</sub>
Pr(NO <sub>3</sub> ) <sub>3</sub>	Gd(NO <sub>3</sub> ) <sub>3</sub>	RbCl	CsCl	RuCl <sub>3</sub>
RhCl <sub>3</sub>	PdCl <sub>2</sub>	SbCl <sub>3</sub>	GeF <sub>4</sub>	AsCl <sub>3</sub>

and Br<sup>-</sup>, I<sup>-</sup> and TeO<sub>3</sub><sup>2-</sup> as the sodium salts and the ammonium salt of MoO<sub>4</sub><sup>2-</sup>,

only thorium, uranyl, tin, antimony, zirconyl, rubidium, cesium, arsenic and iodine gave  $R_F$  values other than zero. Fig. 1 shows the  $R_F$  values of the above ions as a function of nitric acid concentration.

Other ions spotted were:

Pb(NO <sub>3</sub> ) <sub>2</sub>	KNO <sub>3</sub>	Mg(NO <sub>3</sub> ) <sub>2</sub>	Co(NO <sub>3</sub> ) <sub>2</sub>	Cu(NO <sub>3</sub> ) <sub>2</sub>
Al(NO <sub>3</sub> ) <sub>3</sub>	Fe(NO <sub>3</sub> ) <sub>3</sub>	Ni(NO <sub>3</sub> ) <sub>2</sub>	Cr(NO <sub>3</sub> ) <sub>3</sub>	Bi(NO <sub>3</sub> ) <sub>3</sub>
Hg(NO <sub>3</sub> ) <sub>2</sub>	Be(NO <sub>3</sub> ) <sub>2</sub>	TiNO <sub>3</sub>	Ca(NO <sub>3</sub> ) <sub>2</sub>	Mn(NO <sub>3</sub> ) <sub>2</sub>
AuCl <sub>3</sub>	H <sub>2</sub> PtCl <sub>6</sub>	VCl <sub>3</sub>	TiCl <sub>3</sub>	

and the sodium salts of Cl<sup>-</sup>, SeO<sub>3</sub><sup>2-</sup> and WO<sub>4</sub><sup>2-</sup>,

of which only bismuth, thallium, potassium, mercury and gold gave  $R_F$  values other than zero. The corresponding curves are plotted in Fig. 2.

Chromatograms were run in 8 *M* and 10 *M* nitric acid-MIBK mixtures, after they had decomposed. It is significant that the great majority of the ions tested gave high  $R_F$  values in these solutions, although their  $R_F$  values in the same solutions, but

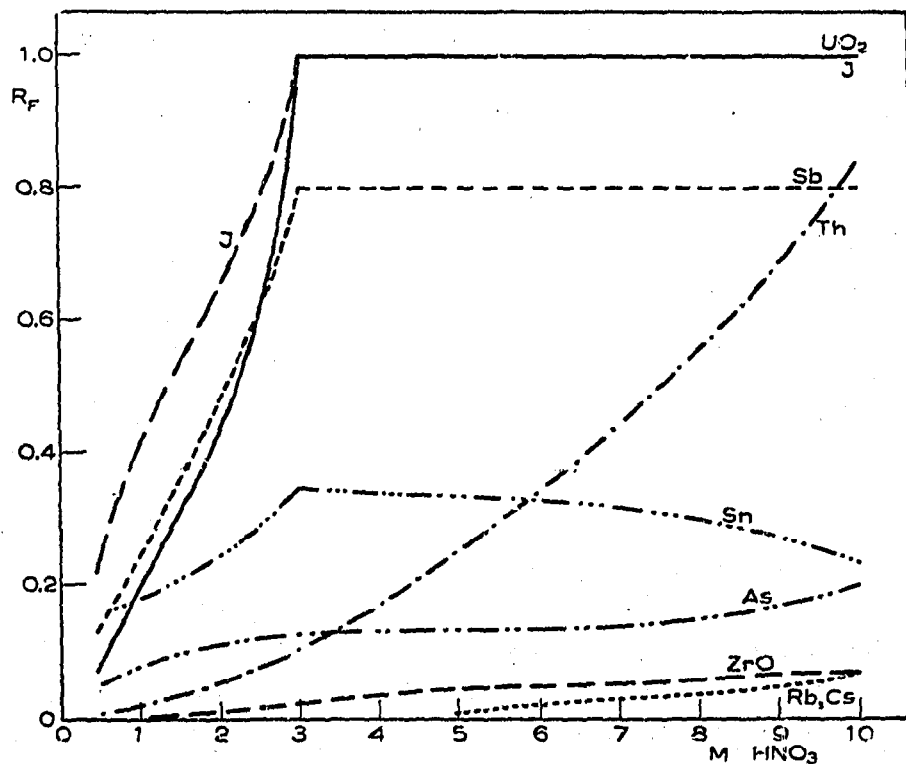


Fig. 1.  $R_F$  values of ions plotted against molarity of nitric acid in MIBK- $\text{HNO}_3$  system.

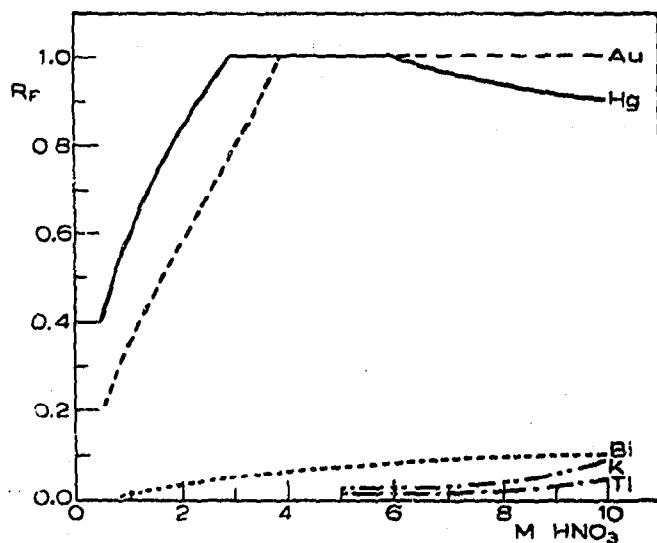


Fig. 2.  $R_F$  values of ions plotted against molarity of nitric acid in MIBK- $\text{HNO}_3$  system.

with unoxidized MIBK, were zero. The results with these decomposed solvents were not reproducible and calculation of  $R_F$  values would be valueless.

#### DISCUSSION

Nitrate complexing of metals in aqueous solutions is usually small in comparison with complexing by other ligands. In solvent extraction processes of metals with nitrates

advantage is taken of the varying extent to which the elements form nitrate-complexes which are more soluble and therefore extractable by the organic solvent. Since  $R_F$  values are related to the partition coefficient by the equation

$$a = \frac{A_L}{A_S} \left( \frac{1}{R_F} - 1 \right)$$

where  $A_L/A_S$  is a constant for any solvent system<sup>6</sup>, we can compare our results with those known from solvent extraction processes. In extraction processes, using MIBK-HNO<sub>3</sub> systems, the elements which tend to be extracted along with uranium, plutonium and thorium are cerium, zirconium, niobium, iodine and ruthenium<sup>7</sup>. Our experiments show that ter- and tetravalent cerium both have  $R_F$  values equal to zero at all the concentrations tested. This phenomenon is probably connected with the reduction of tetravalent cerium to the non-extractable trivalent state by the filter paper. The  $R_F$  values of zirconium nitrate are only very low. Iodine is very extractable. Furthermore, antimony and bivalent tin show high  $R_F$  values, while arsenic and to some extent rubidium and cesium exhibit some extractability at higher nitric acid concentration. Mercury when present can cause some interference.

The high extraction capacity of oxidized MIBK in contact with higher concentrations of aqueous nitric acid solutions must be emphasized.

#### SUMMARY

The  $R_F$  values of a number of inorganic ions were measured in nine different mixtures of methyl isobutyl ketone with nitric acid. The majority of the ions investigated were not extracted by these mixtures ( $R_F = 0$ ). The oxidation of the ketone by concentrated nitric acid and its effect upon the extraction capacity of the ketone has been discussed. The distribution coefficient of nitric acid between water and methyl isobutyl ketone has been redetermined.

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