

REVERSED-PHASE PAPER CHROMATOGRAPHY OF SOME CATIONS WITH TWO NITROPHENYLTHIOPHOSPHATE DERIVATIVES AS STATIONARY PHASES

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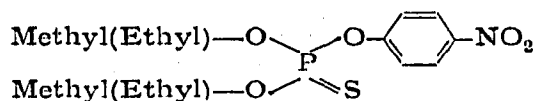
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Many organophosphorus compounds, such as the well-known tri-butyl phosphate, tri-butyl phosphine oxide, and di(2-ethylhexyl)orthophosphoric acid, have been shown to play an outstanding role in solvent extraction of inorganic ions, owing to the solvation properties of the phosphoryl group $P=O$.

HANDLEY AND DEAN¹ reported that, when the $P=O$ group was substituted in some compounds by a $P=S$ group, special selectivity characteristics could be achieved, as in the case of the octyl thiophosphates or butyl thiophosphates, with silver and mercury in a nitrate medium.

In our laboratory the properties of some commercial thiophosphate derivatives were investigated. As already stated elsewhere, a considerable amount of information on the behaviour of a liquid-liquid system can be obtained through a reversed-phase chromatographic technique². Therefore, this method was adopted for a rapid study of two products, namely methylparathion and ethylparathion. Methylparathion (O,O-dimethyl O-*p*-nitrophenyl thiophosphate, mol. wt. 263, sp. gr. 1.36) and ethylparathion (O,O-diethyl O-*p*-nitrophenyl thiophosphate, mol. wt. 291, sp. gr. 1.26), are liquid insecticides, nearly insoluble in water, with the structural formula:



The R_F values obtained by eluting a spot of a given cation with a given aqueous phase on a paper previously treated with a given extractant, can be related to the extraction coefficient E_a^0 for the same cation in the analogous liquid-liquid system, by the equation

$$\log E_a^0 = \log \left(\frac{1}{R_F} - 1 \right) + \text{constant}$$

where the constant depends on the experimental conditions. The main advantage of the chromatographic technique is the practicability of obtaining basic information on the extraction behaviour in a very short time.

EXPERIMENTAL

The insecticides used in the present investigation were technical grade products obtained from different sources which are listed in Table I. During this work no difference among them was noticed with respect to their extraction behaviour.

The paper used was Whatman No. 1, CRL/1 type, which enabled us to carry out a great number of simultaneous elutions running a front of about 9 cm. The reagents and the solvents used were C. Erba R.P. products, supplied by C. Erba (Milan).

TABLE I
COMPOUNDS USED AND THEIR SOURCES

<i>Compound</i>	<i>Source</i>
Methylparathion, 80 %	Bombrini Parodi-Delfino (Rome)
Ethylparathion, 94 %	Bombrini Parodi-Delfino (Rome)
Methylparathion, techn. grade	Montecatini (Milan)
Ethylparathion, techn. grade	Montecatini (Milan)
Methylparathion, 80 %	Cheminova (Denmark), supplied by Nymco (Milan)
Ethylparathion, 98 %	Cheminova (Denmark), supplied by Nymco (Milan)

Solutions for the paper treatment were obtained by diluting parathion with toluene; the already mentioned molecular weights and specific gravities for the pure products were used for calculations.

The diluted technical product was usually purified by treating it with twice its volume of a 5 % Na_2CO_3 solution: this treatment was repeated until the aqueous layer remained colourless after shaking for 5 min.

After purification, the extractant solution was washed with water, and then equilibrated with twice its volume of a 1 *M* nitric acid solution. The paper was treated as described previously³. The apparatus for the ascending development has also been described already⁴.

Drops containing from $1 \cdot 10^{-7}$ to $5 \cdot 10^{-6}$ equivalents of a metal ion, depending on the sensitivity attainable by the detection method, were individually applied on the paper; they were taken from solutions to which, when necessary, enough nitric acid had been added to prevent hydrolysis.

At the beginning, an investigation was carried out to obtain some preliminary information on the system. The ions chosen to be eluted were among those reported by HANDLEY AND DEAN¹ and by HANDLEY⁵ as being extractable by thio-organophosphorus compounds. A few additional representative ions were investigated by us. Thus, the behaviour of titanium(IV), chromium(III), iron(III), copper(II), gallium(III), palladium(II), silver(I), cadmium(II), tin(II), gold(III), and mercury(II) were investigated, using nitric acid at various concentrations as the eluent. After the elution, the spots were detected by spraying the paper with a 0.1 % solution of quercetin in 95 % ethanol for Ti, Ga and Sn; with 0.1 % diphenylcarbazine for Cr; with 0.1 % 8-hydroxyquinoline for Fe and Cu; and with a 0.1 % solution of dithizone in chloroform for the other cations.

RESULTS AND DISCUSSION

At the early stage of the work, unpurified ethylparathion was used. When the paper was treated with concentrated solutions of the product as supplied it was nearly hydrorepellent, and for this reason very dilute solutions of parathion were used, namely 0.04 *M* and 0.02 *M* in toluene. Because of the low capacity of the stationary phase, due to the small amount of extractant present on the paper, the spots after the elution were often very large, and thus the R_F values obtained had an appreciable uncertainty.

Results of this preliminary investigation are reported in Table II as R_F values for the individual cations at the corresponding nitric acid concentration in the eluent. For paper treated with 0.04 *M* ethylparathion, two R_F values are reported for palladium; under these conditions this cation showed a double spot. When the paper was treated with the more dilute solution, only one spot was visible, the R_F of which is reported in the table.

TABLE II

R_F VALUES FOR SOME CATIONS AS FUNCTIONS OF THE MOLARITY OF HNO_3 AS ELUENT
Paper treated with 0.02 *M* and 0.04 *M* ethylparathion in toluene. Operating temperature $24 \pm 1^\circ$.

Ethylparathion molarity	Cation	R_F	Molarity of HNO_3						
			0.0001	0.001	0.01	0.1	1.0	5.0	10.0
0.02	Ti ⁴⁺	0.94	0.94	0.95	0.96	0.82	0.82	0.75	0.68
	Cr ³⁺	0.92	0.92	0.95	0.92	0.95	0.92	0.92	0.92
	Fe ³⁺	0.44	0.72	0.68	0.95	0.95	0.90	0.88	0.82
	Cu ²⁺	0.92	0.92	0.92	0.95	0.94	0.92	0.94	0.95
	Ga ³⁺	0.91	0.91	0.91	0.97	0.88	0.90	0.95	0.71
	Pd ²⁺	0.80	0.79	0.44	0.82	0.85	0.90	0.14	0.37
	Ag ¹⁺	0.00	0.26	0.57	0.90	0.92	0.95	0.95	0.92
	Cd ²⁺	0.87	0.87	0.87	0.87	0.87	0.87	0.88	0.87
	Sn ²⁺	—	0.84	0.88	0.82	0.80	0.74	0.73	0.76
	Au ³⁺	0.62	0.67	—	0.70	0.22	0.42	0.67	0.63
	Hg ²⁺	0.74	0.70	0.70	0.71	0.71	0.75	0.77	0.81
	0.04	Ti ⁴⁺	0.95	0.97	0.95	0.95	0.97	0.95	0.90
Cr ³⁺		0.92	0.95	0.92	0.95	0.95	0.85	0.82	0.76
Cu ²⁺		0.92	0.95	0.92	0.92	0.95	0.97	0.95	0.92
Ga ³⁺		0.92	0.92	0.92	0.93	0.92	0.94	0.94	0.70
Pd ²⁺		0.50	0.57	0.60	0.62	0.61	0.70	0.73	0.82
		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.31
Ag ¹⁺		0.00	0.00	0.00	0.45	0.79	0.95	0.92	0.95
Cd ²⁺		0.34	0.50	0.80	0.95	0.92	0.95	0.70	0.65
Sn ²⁺		0.92	0.96	0.96	0.97	0.82	0.77	0.75	0.62
Au ³⁺		0.00	0.00	0.00	0.00	0.00	0.06	0.77	0.82
Hg ²⁺		0.50	0.63	0.58	0.62	0.62	0.63	0.77	0.70

The low R_F values for iron in the lowest range of the nitric acid concentration are attributable to partial hydrolysis; on the other hand, the lowering of R_F values of nearly all cations at the higher nitric acid concentrations may be ascribed to the dehydration phenomena of the ions which enhance retention, as already found in

other chromatographic systems. However, the presence of parathion on the paper was undoubtedly responsible for the retention of palladium, silver, cadmium, gold, and mercury. The investigation was therefore continued by considering only the five above mentioned cations.

The paper treated with purified methylparathion and ethylparathion was found to be far more wettable than the paper treated with the unpurified products. It was then possible to treat the paper with more concentrated solutions, namely 1 *M* in toluene for both compounds. Because of the higher capacity of stationary phase thus achieved, the spots obtained after the elutions were sufficiently small and very reproducible.

Representative R_F values obtained by eluting palladium, silver, cadmium, gold, and mercury with nitric acid at various concentrations on paper treated with 1 *M* methylparathion and ethylparathion are collected in Table III and are plotted in Fig. 1 against the logarithm of the nitric acid concentration.

TABLE III

R_F VALUES FOR PALLADIUM, SILVER, CADMIUM, GOLD AND MERCURY AS FUNCTIONS OF THE MOLARITY OF HNO_3 AS ELUENT

Paper treated with 1.0 *M* methylparathion or ethylparathion in toluene. Operating temperature $24 \pm 1^\circ$.

Parathion Cation used		R_F												
		Molarity of HNO_3												
		0.0001	0.0005	0.001	0.005	0.01	0.05	0.1	0.5	1.0	5.0	8.0	10.0	14.7
Methyl	Pd ²⁺	0.00	0.05	0.05	0.00	0.00	0.00	0.00	0.00	0.08	0.00	0.00	0.00	—
	Ag ¹⁺	0.00	0.19	0.25	0.20	0.17	0.15	0.18	0.16	0.18	0.25	0.28	0.30	—
	Cd ²⁺	0.10	0.20	0.25	0.55	0.64	0.77	0.79	0.85	0.82	0.95	0.97	0.95	—
	Au ³⁺	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.10	0.15	0.25	—
	Hg ²⁺	0.60	0.62	0.61	0.61	0.62	0.67	0.68	0.66	0.67	0.82	0.88	0.67	—
		Molarity of HNO_3												
		0.0001	0.001	0.002	0.005	0.02	0.1	0.2	1.0	5.0	8.0	10.0	12.0	14.7
Ethyl	Pd ²⁺	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.08
	Ag ¹⁺	0.00	0.00	0.00	0.00	0.00	—	—	0.00	0.32	—	0.60	0.84	0.82
	Cd ²⁺	0.00	0.25	0.55	0.76	—	0.90	0.83	0.85	0.95	0.95	0.97	0.92	0.87
	Au ³⁺	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Hg ²⁺	0.47	0.45	0.46	0.45	0.47	0.45	0.46	0.48	0.50	0.25	0.13	0.10	0.16

In Fig. 1, the behaviour at low nitric acid concentrations was omitted when the R_F in this range had the same value as for 1 *M* acid.

Data for paper treated with methylparathion and eluted with nitric acid at concentrations higher than 10 *M* are not reported, since at these concentrations of eluent the methylparathion present on the paper was washed away by the aqueous phase.

No attempt was made to explain the mechanism of retention, since for such purposes more than the results obtained with this system would be necessary. The

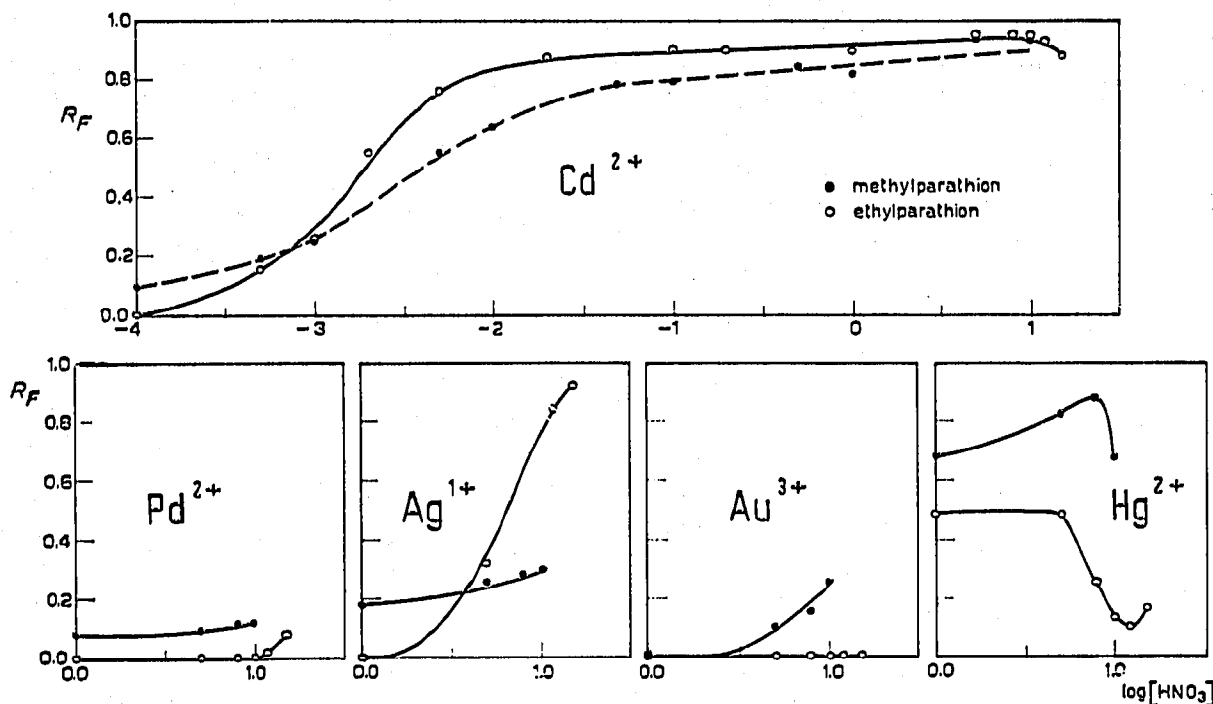


Fig. 1. R_F values for cadmium, palladium, silver, gold, and mercury plotted vs. \log molarity HNO_3 . Paper treated with 1 M methylparathion and 1 M ethylparathion in toluene. Operating temperature $24 \pm 1^\circ$.

experimental evidence, however, showed that both methylparathion and ethylparathion possess a retention power when on the paper, which is undoubtedly related to an analogous extraction power in the liquid-liquid systems.

With the aim of checking the chromatographic results, some liquid-liquid extraction experiments were planned. Unfortunately, after this chromatographic investigation was accomplished, our parathion specimens were almost completely used up. Nevertheless, some preliminary experiments on silver were possible, and the extraction properties of both compounds were confirmed. Data collected in Table IV show that a certain dependence exists between percentage extraction and the concentration of silver in the aqueous phase; but this feature was not investigated further.

TABLE IV

EXTRACTION OF SILVER BY METHYLPARATHION AND ETHYLPARATHION IN TOLUENE FROM AQUEOUS NITRIC ACID SOLUTIONS

Organic phase: 5 ml of extractant 1 M in toluene. Aqueous phase: 5 ml of nitric acid at various concentrations containing variable amounts of silver. Shaking time: 30 min. Temperature: $24 \pm 1^\circ$.

Extractant	Molarity of HNO_3	μg Ag in the aqueous phase		% Ag extracted
		Before extraction	After extraction	
Methylparathion	0.0001	62.0	38.0	44
Ethylparathion	0.0001	12.2	9.8	31
Ethylparathion	0.0001	30.4	15.7	43
Ethylparathion	0.0001	152	60.0	60
Ethylparathion	0.4	152	78.0	48

During the present work, Emmatos (O,O-dimethyldithiophosphate of diethylmercaptosuccinate, produced by BPD, Rome) was also tested in liquid-liquid extractions. An 8 % solution of this compound in ethyl ether was found to extract completely 1 mg/ml of silver from a 3 M nitric acid solution, with a 1:1 volume phase ratio.

From the results of the purely preliminary research reported here, it was felt that further investigations would be worthwhile on the use of thiophosphorus industrial insecticides as extractants in inorganic chemistry. Although the high toxicity of these compounds is undoubtedly a disadvantage for their use in the laboratory, on the other hand they are currently produced by industrial processes and thus are relatively cheap.

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SUMMARY

Two industrial thiophosphorus insecticides, namely methylparathion and ethylparathion, were used as impregnants for paper for reversed-phase chromatography of several cations with nitric acid as the eluent.

Palladium, silver, cadmium, gold, and mercury were shown to be more or less retained by the stationary phase. The behaviour of silver was checked also by liquid-liquid extraction.

The use of the above mentioned insecticides, and of Emmatos (malathion) as liquid-liquid extractants was suggested.

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