

CHROM. 3457

# THIN-LAYER CHROMATOGRAPHY OF METAL IONS ON ALGINIC ACID

## PART II

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(First received November 16th, 1967; modified February 20th, 1968)

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### SUMMARY

The  $R_F$  values of 41 elements, some in two oxidation states, have been determined by TLC on alginic acid. The effect of the nature and concentration of the acids employed as eluents was extensively investigated.

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### INTRODUCTION

In a previous paper<sup>1</sup> the characteristics and the use of alginic acid in TLC have been described. Since preliminary results appeared promising, the chromatographic behavior of most elements has been investigated. To correlate the chromatographic characteristics of the elements, they have been examined according to the groups of the periodic table.

### EXPERIMENTAL

The thin layers were prepared from a slurry which was applied to the plates in the usual way with commercially available equipment manufactured by "Quickfit Instruments". The spreader blade was set to give a layer 250  $\mu$  thick.

#### *Solutions*

The solutions of the elements were prepared and used as previously described<sup>1</sup>.

#### *Detection reagents*

- (1)  $\text{NH}_4\text{HS}$ : 0.2 *N* solution.
- (2) 8-Hydroxyquinoline: 1% solution in ethanol followed by exposure to ammonia vapors.
- (3) Morin: 1% solution in methanol.
- (4) Kojic acid and 8-hydroxyquinoline mixture: 0.1 g of kojic acid and 0.5 g of 8-hydroxyquinoline in 100 ml of 60% alcohol followed by exposure to ammonia vapors.
- (5) Chromotropic acid: 5% solution in 1:1 sulfuric acid.

- (6) Potassium iodide: 5 % solution in water.
- (7) Hydrogen peroxide: freshly prepared 3 % solution in 2 *N* NaOH, followed by spraying with a 0.5 % benzidine solution in 10 % acetic acid.
- (8) Stannous chloride-potassium iodide mixture: solution 1 : 1 by volume of 2 % stannous chloride in 10 % HCl and 2 % potassium iodide in water.
- (9) Mixed acids: concentrated HClO<sub>4</sub>, HNO<sub>3</sub>, and H<sub>3</sub>PO<sub>4</sub>.
- (10) Silver nitrate: 0.1 *M* solution in water.
- (11) Dithizone: 1 % solution in chloroform.
- (12) Sodium rhodizonate: freshly prepared saturated aqueous solution.

#### Measurement of $R_F$ values

The  $R_F$  values were determined as previously described<sup>1</sup>. All values, unless otherwise stated, are measured at room temperature (19–22 °C).

#### Reproducibility

Although the solvent front was irregular, the results of repeated experiments showed good agreement ( $\pm 0.02$ – $0.08$  in  $R_F$  value). In a few cases, reported in the remarks to the tables, altered  $R_F$  values have been obtained.

#### Eluents

HCl, HNO<sub>3</sub>, HClO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub>, CH<sub>3</sub>COOH, (COOH)<sub>2</sub> of variable concentration. The concentration range of various acids was between 10<sup>-2</sup> and 1 *M*. Within these

TABLE I  
 $R_F$  VALUES OF ELEMENTS ON ALGINIC ACID THIN LAYERS

Eluent	Moles/l	Cu(II)	Ag(I)	Au(III)
(COOH) <sub>2</sub>	0.01	0.00	0.00	0.10 ± 0.10
	0.1	0.00	0.00	0.12 ± 0.12
	0.5	0.00	0.00	0.14 ± 0.14
CH <sub>3</sub> COOH	1	0.00	0.00	(—) <sup>a</sup>
HCl	0.01	0.02 ± 0.02	0.00	0.26 ± 0.09
	0.1	0.34 ± 0.04	0.00	0.35 ± 0.08
	1	0.95 ± 0.05	0.00	0.40 ± 0.08
H <sub>3</sub> PO <sub>4</sub>	0.01	0.00	0.00	0.14 ± 0.10
	0.1	0.10 ± 0.06	0.20 ± 0.04	0.16 ± 0.11
	1	0.70 ± 0.06	0.43 ± 0.04	0.18 ± 0.11
HNO <sub>3</sub>	0.01	0.00	0.07 ± 0.04	0.14 ± 0.10
	0.1	0.33 ± 0.05	0.42 ± 0.04	0.18 ± 0.09
	0.5	0.94 ± 0.06	0.64 ± 0.04	0.23 ± 0.10
HClO <sub>4</sub>	0.01	0.00	0.06 ± 0.04	0.15 ± 0.10
	0.1	0.33 ± 0.04	0.37 ± 0.04	0.20 ± 0.12
	1	0.94 ± 0.06	0.60 ± 0.04	0.30 ± 0.13
Amount (μg)		5	5	3
Detecting reagents		1	1	b

<sup>a</sup> (—) = diffuse.

<sup>b</sup> Purple.

TABLE II

 $R_F$  VALUES OF ELEMENTS ON ALGINIC ACID THIN LAYERS

Eluent	Moles/l	Be(II)	Mg(II)	Ca(II)	Sr(II)	Ba(II)
(COOH) <sub>2</sub>	0.01	0.06 ± 0.06	0.06 ± 0.06	n.d. <sup>a</sup>	0.00	0.00
	0.1	0.80 ± 0.07	0.72 ± 0.06	n.d.	0.21 ± 0.04	0.08 ± 0.04
	0.5	0.94 ± 0.06	0.94 ± 0.06	n.d.	n.d.	0.20 ± 0.04
CH <sub>3</sub> COOH	1	0.04 ± 0.04	0.06 ± 0.06	0.00	0.00	0.00
HCl	0.01	0.05 ± 0.05	0.09 ± 0.09	0.00	0.00	0.00
	0.1	0.63 ± 0.07	0.68 ± 0.06	0.44 ± 0.05	0.32 ± 0.04	0.08 ± 0.04
	1	0.93 ± 0.07	0.94 ± 0.06	0.95 ± 0.05	0.68 ± 0.05	0.30 ± 0.04
H <sub>3</sub> PO <sub>4</sub>	0.01	0.05 ± 0.05	0.05 ± 0.05	0.00	0.00	0.00
	0.1	n.d.	0.29 ± 0.06	0.12 ± 0.05	0.10 ± 0.05	0.03 ± 0.03
	1	n.d.	0.94 ± 0.06	n.d.	0.48 ± 0.05	0.15 ± 0.04
HNO <sub>3</sub>	0.01	0.04 ± 0.04	0.08 ± 0.08	0.00	0.00	0.00
	0.1	0.63 ± 0.07	0.67 ± 0.06	0.44 ± 0.05	0.32 ± 0.05	0.08 ± 0.04
	0.5	0.94 ± 0.06	0.94 ± 0.06	0.93 ± 0.07	0.64 ± 0.05	0.25 ± 0.04
HClO <sub>4</sub>	0.01	0.05 ± 0.05	0.08 ± 0.08	0.00	0.00	0.00
	0.1	0.62 ± 0.07	0.68 ± 0.06	0.43 ± 0.05	0.31 ± 0.05	0.07 ± 0.04
	1	0.93 ± 0.07	0.94 ± 0.06	0.95 ± 0.05	0.68 ± 0.05	0.30 ± 0.05
Amount (μg)		0.7	1	7	15	10
Detecting reagents		2	2	2	12	12

<sup>a</sup> n.d. = not determined.

TABLE III

 $R_F$  VALUES OF ELEMENTS ON ALGINIC ACID THIN LAYERS

Eluent	Moles/l	Zn(II)	Cd(II)	Hg(II)
(COOH) <sub>2</sub>	0.01	0.00	0.00	0.66 ± 0.08
	0.1	0.32 ± 0.05	0.33 ± 0.04	0.69 ± 0.07
	0.5	0.96 ± 0.04	0.95 ± 0.05	0.75 ± 0.07
CH <sub>3</sub> COOH	1	0.00	0.00	0.64 ± 0.06
HCl	0.01	0.02 ± 0.02	0.03 ± 0.03	0.79 ± 0.06
	0.1	0.58 ± 0.05	0.72 ± 0.05	0.89 ± 0.08
	1	0.94 ± 0.06	0.94 ± 0.06	0.93 ± 0.07
H <sub>3</sub> PO <sub>4</sub>	0.01	0.00	0.00	0.65 ± 0.05
	0.1	0.14 ± 0.04	0.14 ± 0.04	0.68 ± 0.06
	1	0.94 ± 0.06	0.95 ± 0.05	0.72 ± 0.08
HNO <sub>3</sub>	0.01	0.02 ± 0.02	0.02 ± 0.02	0.64 ± 0.06
	0.1	0.54 ± 0.05	0.53 ± 0.04	0.74 ± 0.06
	0.5	0.94 ± 0.06	0.95 ± 0.05	0.76 ± 0.06
HClO <sub>4</sub>	0.01	0.02 ± 0.02	0.02 ± 0.02	0.63 ± 0.06
	0.1	0.55 ± 0.05	0.53 ± 0.04	0.73 ± 0.07
	1	0.94 ± 0.06	0.95 ± 0.05	0.90 ± 0.10
Amount (μg)		2.3	1.8	5
Detecting reagents		2	11	11

TABLE IV

 $R_F$  VALUES OF ELEMENTS ON ALGINIC ACID THIN LAYERS

Eluent	Moles/l	Al(III)	Ga(III)	In(III)	Tl(I)
(COOH) <sub>2</sub>	0.01	0.93 ± 0.07	0.93 ± 0.07	0.15 ± 0.05	0.05 ± 0.04
	0.1	0.94 ± 0.06	0.94 ± 0.06	n.d. <sup>b</sup>	0.17 ± 0.04
	0.5	0.94 ± 0.06	0.94 ± 0.06	n.d.	0.25 ± 0.04
CH <sub>3</sub> COOH	1	0.00	0.00	0.00	0.00
HCl	0.01	0.05 ± 0.05	0.00	0.03 ± 0.03	0.08 ± 0.04
	0.1	(—) <sup>a</sup>	0.22 ± 0.06	0.40 ± 0.06	(—)
	1	0.94 ± 0.06	0.94 ± 0.06	0.94 ± 0.06	0.00
H <sub>3</sub> PO <sub>4</sub>	0.01	0.04 ± 0.04	0.00	0.00	0.06 ± 0.04
	0.1	0.24 ± 0.08	0.08 ± 0.06	0.18 ± 0.06	0.09 ± 0.04
	1	0.94 ± 0.06	0.94 ± 0.06	0.94 ± 0.06	0.22 ± 0.04
HNO <sub>3</sub>	0.01	0.05 ± 0.05	0.00	0.00	0.05 ± 0.04
	0.1	(—)	0.22 ± 0.06	0.03 ± 0.03	0.21 ± 0.04
	0.5	0.94 ± 0.06	0.93 ± 0.07	0.56 ± 0.07	0.32 ± 0.04
HClO <sub>4</sub>	0.01	0.05 ± 0.05	0.00	0.00	0.05 ± 0.04
	0.1	(—)	0.21 ± 0.06	0.04 ± 0.04	0.20 ± 0.04
	1	0.94 ± 0.06	0.94 ± 0.06	0.94 ± 0.06	0.36 ± 0.04
Amount (μg)		0.5	1.5	2.5	10
Detecting reagents		2	3	3	1

<sup>a</sup> (—) = diffuse.<sup>b</sup> n.d. = not determined.

limits the  $R_F$  values of most of the elements examined cover a wide range. When the acid concentration is below 0.01 *M* the  $R_F$  values do not vary appreciably.

## RESULTS AND DISCUSSION

### General remarks

Most of the elements examined gave well defined spots. For the following ions: Au(III), Mg(II), Be(II), Al(III), Ti(IV), W(VI), Fe(III), Pd(II), and Th(IV) the spots obtained were more or less diffuse depending upon the ion and the medium in which the chromatogram was developed. Difficulties in detection of the ions were not, in general, encountered, except in a few cases discussed under the remarks to the tables. The development distance of the solvent front was always approx. 10 cm; the development time was approx. 35–40 min.

### Comments on the tables

*Table I.* The spot of Au(III) is very diffuse in several media excepting hydrochloric acid, in which a fairly well defined spot is obtained. This behavior is related to the partial reduction of gold by alginic acid. Au(III) shows up as a purple spot so that there is no need for a detecting agent. The color intensity increases by heating the chromatoplates at 80°.

*Table II.* Owing to the considerable stability of the compound formed, Ca(II) is not detected and the  $R_F$  values are not reported for phosphoric and oxalic acid media. In some respects, Sr(II) behaves like Ca(II). However, detection of Sr(II) is possible even in a phosphoric acid medium on increasing the amount of the element. This procedure fails in 0.5 M oxalic acid. The detection of Be(II) is also difficult with 0.1 and 1 M  $H_3PO_4$  as developer. The chromatographic behavior of alkaline earths *versus* the concentration of eluent is shown in Fig. 1. With hydrochloric acid concentrations in the eluent higher than 1 M, the  $R_F$  values decrease as the acid concentration increases. Similar behavior has been observed by others<sup>2,3</sup> for several ions, not only with hydrochloric acid but also with other mineral acids.

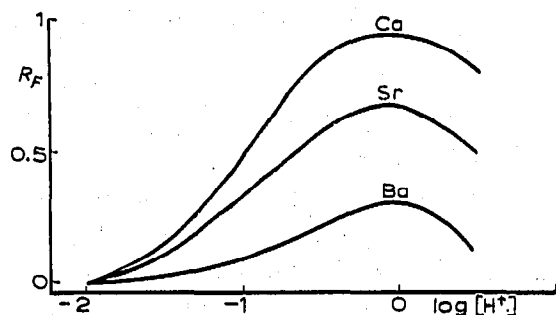


Fig. 1. Relation of  $R_F$  values to  $\log [H^+]$  for Ba, Sr, Ca. Eluent: HCl.

TABLE V

$R_F$  VALUES OF ELEMENTS ON ALGINIC ACID THIN LAYERS

Eluent	Moles/l	Ge(IV)	Sn(IV)	Pb(II)
(COOH) <sub>2</sub>	0.01	(-) <sup>a</sup>	0.00	0.00
	0.1	0.94 ± 0.06	0.00	0.00
	0.5	0.94 ± 0.06	0.00	0.00
CH <sub>3</sub> COOH	1	(-)	0.00	0.00
HCl	0.01	0.94 ± 0.06	0.00	0.00
	0.1	0.94 ± 0.06	0.00	0.03 ± 0.03
	1	0.94 ± 0.06	0.00	0.37 ± 0.03
H <sub>3</sub> PO <sub>4</sub>	0.01	(-)	0.00	0.00
	0.1	(-)	0.00	0.00
	1	(-)	0.00	0.06 ± 0.03
HNO <sub>3</sub>	0.01	0.94 ± 0.06	0.00	0.00
	0.1	0.94 ± 0.06	0.00	0.00
	0.5	0.94 ± 0.06	0.00	0.10 ± 0.03
HClO <sub>4</sub>	0.01	0.94 ± 0.06	0.00	0.00
	0.1	0.94 ± 0.06	0.00	0.00
	1	0.94 ± 0.06	0.00	0.14 ± 0.03
Amount (μg)		10	10	5
Detecting reagents		3	4	1

<sup>a</sup> (-) = diffuse.

*Table III.* From a chromatographic point of view, there are no differences between Zn(II) and Cd(II) in the various media. Their separation is only possible in 0.1 *M* HCl; in this medium, owing to the relative stability of their chloro-complexes the behavior of Cd(II) is different from that of Zn(II). Hg(II) is little influenced by the nature of the acid; only in hydrochloric acid is the complexing action of the chloride ion evident. In this medium, the  $R_F$  values are more reproducible. In the case of Cd(II) and Hg(II) the chlorides were used and the initial solutions were acidified with HCl.

*Table IV.* The detection of In(III) fails in 0.1 and 0.5 *M* oxalic acid. Separation of Al(III), Ga(III) and In(III) is possible in several media. For these elements the extent of retention increases as the atomic number of the ion increases.

The behavior of Tl(I) with HCl as developer is dependent on the solubility of TlCl, and with a hydrochloric acid eluent concentration of  $> 0.25$  moles/l, the Tl(I) spot remains at the origin.

*Table V.* In the case of Ge(IV), it is advisable, if  $H_3PO_4$  is used as eluent, to spray the plate with 3 *M* HCl before detecting it with the reagent solution. The  $R_F$  values of Sn(IV) are in agreement with the formation of stannic acid and/or basic salts with alginic acid as shown by SCHWEIGER<sup>4</sup>. In the case of Sn(IV) and Ge(IV) the chlorides were used and the initial solutions acidified with HCl. In such a medium both elements are present as very stable chloro-complexes, so that the chromatographic characteristics depend upon the initial complex state of the elements.

TABLE VI

 $R_F$  VALUES OF ELEMENTS ON ALGINIC ACID THIN LAYERS

Eluent	Moles/l	Ti(IV)	Zr(IV)	Th(IV)
(COOH) <sub>2</sub>	0.01	(—) <sup>a</sup>	0.04 ± 0.04	0.00
	0.1	(—)	0.91 ± 0.09	0.00
	0.5	(—)	0.94 ± 0.06	0.00
CH <sub>3</sub> COOH	1	0.91 ± 0.09	0.00	0.00
HCl	0.01	0.91 ± 0.09	0.00	0.00
	0.1	0.92 ± 0.08	0.05 ± 0.05	0.00
	1	0.92 ± 0.08	0.06 ± 0.06	0.74 ± 0.08
H <sub>3</sub> PO <sub>4</sub>	0.01	(—)	0.00	0.00
	0.1	(—)	0.00	0.00
	1	(—)	0.00	0.00
HNO <sub>3</sub>	0.01	0.91 ± 0.09	0.00	0.00
	0.1	0.91 ± 0.09	0.00	0.00
	0.5	0.92 ± 0.08	0.03 ± 0.03	0.26 ± 0.07
HClO <sub>4</sub>	0.01	0.91 ± 0.09	0.00	0.00
	0.1	0.91 ± 0.09	0.00	0.00
	1	0.92 ± 0.08	0.05 ± 0.05	0.48 ± 0.10
Amount (μg)		6	8	15
Detecting reagents		5	2	3

<sup>a</sup> (—) = diffuse.

TABLE VII

 $R_F$  VALUES OF ELEMENTS ON ALGINIC ACID THIN LAYERS

<i>Eluent</i>	<i>Moles/l</i>	<i>As(V)</i>	<i>As(III)</i>	<i>Sb(III)</i>	<i>Bi(III)</i>	<i>V(V)</i>
(COOH) <sub>2</sub>	0.01	0.94 ± 0.06	0.50 ± 0.04	0.06 ± 0.04	0.06 ± 0.03	0.93 ± 0.07
	0.1	0.94 ± 0.06	0.49 ± 0.04	0.50 ± 0.04	0.18 ± 0.04	0.94 ± 0.06
	0.5	0.94 ± 0.06	0.50 ± 0.04	0.73 ± 0.04	0.24 ± 0.06	0.95 ± 0.05
CH <sub>3</sub> COOH	I	0.94 ± 0.06	0.48 ± 0.04	0.00	0.00	0.00
HCl	0.01	0.94 ± 0.06	0.54 ± 0.04	0.00	0.00	0.03 ± 0.03
	0.1	0.94 ± 0.06	0.55 ± 0.04	0.03 ± 0.03	0.03 ± 0.03	0.33 ± 0.05
	I	0.94 ± 0.06	0.52 ± 0.04	0.22 ± 0.03	0.93 ± 0.07	0.95 ± 0.05
H <sub>3</sub> PO <sub>4</sub>	0.01	0.94 ± 0.06	0.45 ± 0.04	0.00	0.00	0.03 ± 0.03
	0.1	0.94 ± 0.06	0.48 ± 0.04	0.05 ± 0.05	0.00	0.22 ± 0.06
	I	0.94 ± 0.06	0.50 ± 0.04	0.30 ± 0.05	0.00	0.93 ± 0.07
HNO <sub>3</sub>	0.01	0.94 ± 0.06	0.47 ± 0.04	0.00	0.00	0.04 ± 0.04
	0.1	0.94 ± 0.06	0.48 ± 0.04	0.03 ± 0.03	0.03 ± 0.03	0.30 ± 0.06
	0.5	0.94 ± 0.06	0.48 ± 0.04	0.05 ± 0.05	0.05 ± 0.05	0.95 ± 0.05
HClO <sub>4</sub>	0.01	0.94 ± 0.06	0.47 ± 0.04	0.00	0.00	0.04 ± 0.04
	0.1	0.94 ± 0.06	0.47 ± 0.04	0.00	0.00	0.31 ± 0.06
	I	0.94 ± 0.06	0.47 ± 0.04	0.03 ± 0.03	0.03 ± 0.03	0.95 ± 0.05
Amount (μg)		7	15	4	3	4
Detecting reagents		6	I	I	I	2

TABLE VIII

 $R_F$  VALUES OF ELEMENTS ON ALGINIC ACID THIN LAYERS

<i>Eluent</i>	<i>Moles/l</i>	<i>Cr(III)</i>	<i>Mo(VI)</i>	<i>W(VI)</i>	<i>U(VI)</i>
(COOH) <sub>2</sub>	0.01	0.06 ± 0.06	0.93 ± 0.07	0.06 ± 0.06	0.56 ± 0.11
	0.1	0.33 ± 0.05	0.94 ± 0.06	0.08 ± 0.08	0.94 ± 0.06
	0.5	0.94 ± 0.06	0.95 ± 0.05	0.11 ± 0.07	0.94 ± 0.06
CH <sub>3</sub> COOH	I	0.00	0.00	0.00	0.00
HCl	0.01	0.00	0.00	0.06 ± 0.06	0.03 ± 0.03
	0.1	0.39 ± 0.05	0.06 ± 0.04	0.08 ± 0.08	0.28 ± 0.05
	I	0.93 ± 0.07	0.37 ± 0.04	0.08 ± 0.08	0.95 ± 0.05
H <sub>3</sub> PO <sub>4</sub>	0.01	0.04 ± 0.04	(-)	(-)	0.03 ± 0.03
	0.1	0.08 ± 0.08	(-)	(-)	0.45 ± 0.04
	I	(-) <sup>a</sup>	0.93 ± 0.07	0.08 ± 0.06	0.94 ± 0.06
HNO <sub>3</sub>	0.01	0.00	0.00	0.05 ± 0.05	0.04 ± 0.04
	0.1	0.38 ± 0.05	0.07 ± 0.07	0.07 ± 0.07	0.21 ± 0.05
	0.5	0.92 ± 0.08	0.22 ± 0.04	0.08 ± 0.08	0.92 ± 0.08
HClO <sub>4</sub>	0.01	0.00	0.00	0.06 ± 0.06	0.03 ± 0.03
	0.1	0.38 ± 0.05	0.07 ± 0.04	0.08 ± 0.08	0.20 ± 0.06
	I	0.94 ± 0.06	0.35 ± 0.05	0.08 ± 0.08	0.93 ± 0.07
Amount (μg)		3	5	9	11
Detecting reagents		7	I	8	2

<sup>a</sup> (-) = diffuse.

TABLE IX

 $R_F$  VALUES OF ELEMENTS ON ALGINIC ACID THIN LAYERS

<i>Eluent</i>	<i>Moles/l</i>	<i>Se(IV)</i>	<i>Te(IV)</i>
(COOH) <sub>2</sub>	0.01	0.95 ± 0.05	0.00
	0.1	0.95 ± 0.05	0.00
	0.5	0.95 ± 0.05	0.05 ± 0.04
CH <sub>3</sub> COOH	I	0.95 ± 0.05	0.00
HCl	0.01	0.95 ± 0.05	0.00
	0.1	0.95 ± 0.05	0.05 ± 0.04
	I	0.95 ± 0.05	0.28 ± 0.04
H <sub>3</sub> PO <sub>4</sub>	0.01	0.95 ± 0.05	0.00
	0.1	0.95 ± 0.05	0.00
	I	0.95 ± 0.05	0.05 ± 0.04
HNO <sub>3</sub>	0.01	0.95 ± 0.05	0.00
	0.1	0.95 ± 0.05	0.05 ± 0.04
	0.5	0.95 ± 0.05	0.16 ± 0.04
HClO <sub>4</sub>	0.01	0.95 ± 0.05	0.00
	0.1	0.95 ± 0.05	0.04 ± 0.04
	I	0.95 ± 0.05	0.26 ± 0.04
Amount (μg)		2	3
Detecting reagents		6	6

TABLE X

 $R_F$  VALUES OF ELEMENTS ON ALGINIC ACID THIN LAYERS

<i>Eluent</i>	<i>Moles/l</i>	<i>Mn(II)</i>	<i>Re(III)</i>
(COOH) <sub>2</sub>	0.01	0.06 ± 0.06	0.68-0.83
	0.1	0.51 ± 0.08	0.68-0.83
	0.5	0.93 ± 0.07	0.68-0.83
CH <sub>3</sub> COOH	I	0.03 ± 0.03	0.68-0.83
HCl	0.01	0.05 ± 0.05	0.68-0.83
	0.1	0.64 ± 0.05	0.68-0.83
	I	0.93 ± 0.07	0.68-0.83
H <sub>3</sub> PO <sub>4</sub>	0.01	0.05 ± 0.05	0.68-0.83
	0.1	0.10 ± 0.10	0.68-0.83
	I	n.d. <sup>a</sup>	0.68-0.83
HNO <sub>3</sub>	0.01	0.04 ± 0.04	0.68-0.83
	0.1	0.63 ± 0.05	0.68-0.83
	0.5	0.93 ± 0.07	0.68-0.83
HClO <sub>4</sub>	0.01	0.04 ± 0.04	0.68-0.83
	0.1	0.64 ± 0.05	0.68-0.83
	I	0.95 ± 0.05	0.68-0.83
Amount (μg)		2	10
Detecting reagents		7	b

<sup>a</sup> n.d. = not determined.<sup>b</sup> Red.



TABLE XI

 $R_F$  VALUES OF ELEMENTS ON ALGINIC ACID THIN LAYERS

Eluent	Moles/l	Fe(III)	Co(II)	Ni(II)
(COOH) <sub>2</sub>	0.01	(-) <sup>a</sup>	0.06 ± 0.04	0.13 ± 0.04
	0.1	0.92 ± 0.08	0.93 ± 0.07	0.93 ± 0.07
	0.5	0.93 ± 0.07	0.95 ± 0.05	0.95 ± 0.05
CH <sub>3</sub> COOH	1	0.04 ± 0.04	0.00	0.00
HCl	0.01	0.05 ± 0.05	0.05 ± 0.04	0.05 ± 0.04
	0.1	0.12 ± 0.09	0.60 ± 0.05	0.59 ± 0.05
	1	0.93 ± 0.07	0.94 ± 0.06	0.95 ± 0.05
H <sub>3</sub> PO <sub>4</sub>	0.01	0.04 ± 0.04	0.06 ± 0.04	0.06 ± 0.04
	0.1	0.24 ± 0.09	0.13 ± 0.04	0.13 ± 0.04
	1	0.93 ± 0.07	0.95 ± 0.05	0.95 ± 0.05
HNO <sub>3</sub>	0.01	0.05 ± 0.05	0.03 ± 0.03	0.03 ± 0.03
	0.1	0.09 ± 0.09	0.55 ± 0.04	0.55 ± 0.04
	0.5	(-)	0.95 ± 0.05	0.95 ± 0.05
HClO <sub>4</sub>	0.01	0.05 ± 0.05	0.03 ± 0.03	0.03 ± 0.03
	0.1	0.10 ± 0.10	0.54 ± 0.04	0.54 ± 0.04
	1	0.92 ± 0.08	0.95 ± 0.05	0.95 ± 0.05
Amount (μg)		1.5	1.5	1.5
Detecting reagents		2	1	1

<sup>a</sup> (-) = diffuse.

*Table VI.* Ti(IV), present in the initial solution as the sulfuric acid complex, is not retained on alginic acid thin layers when weakly complexing acids are used as eluents. In oxalic and in phosphoric acids Ti(IV) is retained more. This behavior is probably due to the conversion of the initial sulfuric complex of Ti(IV) into different ionic species.

*Table VII.* As(V) is not retained on alginic acid thin layers on using acidic eluents. The behavior of P(V) is identical to that of As(V). As(III) shows anomalous

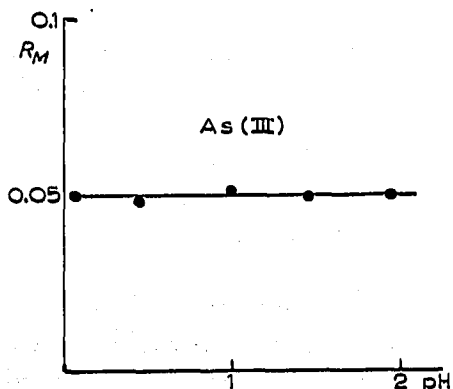
Fig. 2. pH dependence of  $R_M$  values for As (III).

TABLE XII

 $R_F$  VALUES OF ELEMENTS ON ALGINIC ACID THIN LAYERS

Eluent	Moles/l	Pt(IV)	Ir(IV)	Os(IV)	Rh(III)	Pd(II)
(COOH) <sub>2</sub>	0.01	0.95 ± 0.05	0.95 ± 0.05	0.95 ± 0.05	(0.00; 0.23; 0.95)	(—) <sup>a</sup>
	0.1	0.95 ± 0.05	0.95 ± 0.05	0.95 ± 0.05	(0.00; 0.94)	(—)
	0.5	0.95 ± 0.05	0.95 ± 0.05	0.95 ± 0.05	(0.00; 0.94)	(—)
CH <sub>3</sub> COOH	1	0.95 ± 0.05	0.95 ± 0.05	0.95 ± 0.05	(0.00; 0.20; 0.95)	0.06 ± 0.06
HCl	0.01	0.95 ± 0.05	0.95 ± 0.05	0.95 ± 0.05	(0.00; 0.26; 0.95)	0.03 ± 0.03
	0.1	0.95 ± 0.05	0.95 ± 0.05	0.95 ± 0.05	(0.00; 0.95)	(—)
	1	0.95 ± 0.05	0.95 ± 0.05	0.95 ± 0.05	(0.00; 0.95)	(0.00; 0.95)
H <sub>3</sub> PO <sub>4</sub>	0.01	0.95 ± 0.05	0.95 ± 0.05	0.95 ± 0.05	(0.00; 0.28; 0.94)	0.00
	0.1	0.95 ± 0.05	0.95 ± 0.05	0.95 ± 0.05	(0.00; 0.46; 0.95)	0.03 ± 0.03
	1	0.95 ± 0.05	0.95 ± 0.05	0.95 ± 0.05	(0.00; 0.95)	0.08 ± 0.08
HNO <sub>3</sub>	0.01	0.95 ± 0.05	0.95 ± 0.05	0.95 ± 0.05	(0.00; 0.26; 0.95)	0.03 ± 0.03
	0.1	0.95 ± 0.05	0.95 ± 0.05	0.95 ± 0.05	(0.00; 0.95)	0.05 ± 0.05
	0.5	0.95 ± 0.05	0.95 ± 0.05	0.95 ± 0.05	(0.00; 0.95)	0.12 ± 0.12
HClO <sub>4</sub>	0.01	0.95 ± 0.05	0.95 ± 0.05	0.95 ± 0.05	(0.00; 0.25; 0.95)	0.03 ± 0.03
	0.1	0.95 ± 0.05	0.95 ± 0.05	0.95 ± 0.05	(0.00; 0.94)	0.05 ± 0.05
	1	0.95 ± 0.05	0.95 ± 0.05	0.95 ± 0.05	(0.00; 0.95)	(—)
Amount (μg)		5	7	5	0.7	1
Detecting reagents		8	9	10	8	8

<sup>a</sup> (—) = diffuse.

behavior. It is influenced neither by the nature nor by the concentration of the eluent. This fact is probably due to the presence of a neutral species in the initial solution and to the considerable stability of these compounds. According to the opinion of LEDERER AND KERTES<sup>5</sup> the plot obtained in Fig. 2 is characteristic of neutral species. In the case of As(III) the initial solution was acidified with HCl.

*Table VIII.* The separation of Mo(VI) and W(VI) is easily obtained owing to the different solubilities of the corresponding acids in the various media; the exception is in CH<sub>3</sub>COOH and for concentrations of mineral acids in the eluent below 0.5 M. The spots of W(VI) are generally diffuse. Cr(III) and U(VI) behave similarly in every medium, except for phosphoric acid, where U(VI) is present as a soluble phosphoric acid complex and in oxalic acid owing to the different stabilities of the corresponding complexes.

*Table IX.* Se(IV) and Te(IV) are easily separated by the various eluents. The chromatographic behavior is in agreement with the weakly metallic character of Se(IV) and with the stronger metallic properties of Te(IV).

*Table X.* Re(III) shows up as a red spot and there is no need for a detecting agent. The behavior of this ion is similar to As(III) since it is not sensibly influenced by the nature and concentration of the eluent. In the case of Re(III) the chloride was used and the initial solution acidified with HCl.

*Table XI.* The chromatographic behavior of Fe(III) is in agreement with the formation of basic salts with alginic acid<sup>4</sup>. The spots of Fe(III) are generally diffuse. From a chromatographic point of view, the behavior of Co(II) and Ni(II) is similar.

*Table XII.* Pt(IV), Ir(IV) and Os(IV), present in the initial solution as chloro-complexes, are not retained by alginic acid thin layers. In the case of Rh(III), where a variety of chloro-complexes of varying stability are known<sup>6</sup>, three spots are obtained at low acid concentrations in the eluent and two spots with higher acid strengths. In 1 *M* hydrochloric and perchloric acid the main portion of the element is found close to the solvent front while a minor part is found at the origin. In 1 *M* hydrochloric acid the behavior of Pd(II) is similar to that of Rh(III).

#### ACKNOWLEDGEMENT

This work was performed with financial support from C.N.R.

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