# A RAPID METHOD FOR THE QUALITATIVE ANALYSIS OF MIXTURES OF INORGANIC IONS BY PAPER ELECTROMIGRATION

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### INTRODUCTION

Several authors have studied the separation and subsequent identification of inorganic ions by paper electromigration. No attempt will be made to give a complete survey of these researches, as several reviews are available and new ones appear periodically (see ref. 1 and the reviews appearing every second year in *Analytical Chemistry*, e.g. ref. 2).

Generally speaking these researches concern a small number of ions which have been subjected to a preliminary separation by means of a group-reagent. Proposals for the separation by electromigration of mixtures of a large number of ions are rare, and have not been worked out into a scheme of analysis up till now. Recently GROSS<sup>3</sup> studied the electromigration of a large series of ions in formic acid and ammonium carbonate.

We have been looking for a method by which as many ions as possible could be identified by their different path lengths in the supporting electrolyte together with colours or fluorescence developed with suitable reagents.

In preliminary experiments with a group of about ten ions, the following supporting electrolytes were tried: citric acid, oxalic acid, malonic acid (all three in various concentrations), and also tartaric acid, gluconic acid, ammonium citrate and sodium potassium tartrate. Of these, oxalic acid and malonic acid were discarded on account of their tendency to form precipitates with various ions. Solutions of ammonium citrate and sodium potassium tartrate increase the conductance and have an appreciable buffering capacity; this last property is disadvantageous in several identification reactions. Of the remaining acids, citric acid, in  $\mathbf{I} N$  solution, gave the best results.

In the following experiments we studied the behaviour of the ions: Ag<sup>+</sup>, AsO<sub>3</sub><sup>3-</sup>, AsO<sub>4</sub><sup>3-</sup>, Au<sup>3+</sup>, Ba<sup>2+</sup>, Ca<sup>2+</sup>, Cd<sup>2+</sup>, Ce<sup>3+</sup>, Cl<sup>-</sup>, Co<sup>2+</sup>, Cr<sup>3+</sup>, CrO<sub>4</sub><sup>2-</sup>, Cu<sup>2+</sup>, Fe<sup>2+</sup>, Fe<sup>3+</sup>, Ga<sup>3+</sup>, Hg<sup>2+</sup>, In<sup>3+</sup>, K<sup>+</sup>, La<sup>3+</sup>, Li<sup>+</sup>, Mg<sup>2+</sup>, Mn<sup>2+</sup>, MnO<sub>4</sub><sup>-</sup>, MoO<sub>4</sub><sup>2-</sup>, Na<sup>+</sup>, Ni<sup>2+</sup>, Pb<sup>2+</sup>, Sb<sup>3+</sup>, SeO<sub>3</sub><sup>2-</sup>, SeO<sub>4</sub><sup>2-</sup>, Sn<sup>2+</sup>, Sn<sup>4+</sup>, Sr<sup>2+</sup>, TeO<sub>3</sub><sup>2-</sup>, Th<sup>4+</sup>, Ti<sup>4+</sup>, UO<sub>2</sub><sup>2+</sup>, VO<sup>2+</sup>, WO<sub>4</sub><sup>2-</sup>, Y<sup>3+</sup>, Zn<sup>2+</sup>, and Zr<sup>4+</sup>.

The results obtained indicate that, in the medium chosen, a large number of the above-mentioned ions can be identified clearly after electromigration for one hour or less in some cases.

## Apparatus

### EXPERIMENTAL

A number of paper strips (Whatman No. 1 chromatographic paper,  $80 \times 2$  cm) were sandwiched between two flat glass plates, the ends of each strip coinciding with a slit

bored in the upper glass plate. The cathode- and anode-slits were 75 cm apart. They were filled with an agar gel (14 % in 1 N citric acid) to ensure electrical contact between the carbon electrodes and the strips. The gel also served as an absorbent for the products of electrolysis. A cellophane strip between the gel and the paper strips acted as a barrier for the transport of liquid from the former to the latter (see Fig. 1).

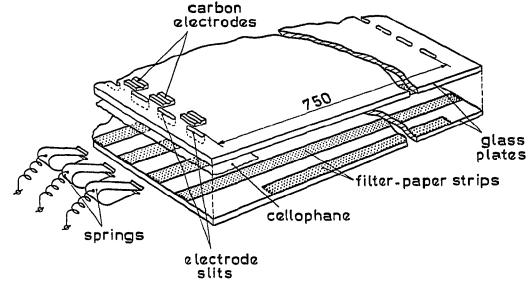


Fig. 1. Electromigration apparatus used in this work.

Evaporation was reduced by inserting two extra strips, soaked in the electrolyte solution, along the long sides of the glass plates and by loading the plates with iron blocks of several kg weight. Contact between the extra paper strips and the cellophane membranes should be avoided.

Control experiments with arabinose showed that electroendosmosis is nil, while the fact that the current in each strip remains fairly constant during the experiments (the applied potential being kept constant) indicates that evaporation is insignificant.

Any high-voltage d.c.-source, capable of maintaining a potential gradient of about 30 V/cm and a current of 2-3 mA in each strip, may be used.

## Reagents and other solutions

Solutions of the ions (of known concentration) in rN citric acid were used. The solutions of the developing reagents, together with the treatment after spraying, are summarized in Table I. The reactions with gases mentioned there, can be performed by hanging the paper strips in  $\therefore$  glass cylinder in which an atmosphere of the particular gas is maintained.

## General procedure

(a) Pretreatment of the paper strips. A pile of 6-10 paper strips was soaked with IN citric acid, and after draining off the surplus liquid the pile of strips was placed between two thick layers of dry filter paper and a brass cylinder was rolled over them twice; the amount of liquid retained by the strips was approximately equal to their own weight. The strips were placed on the lower glass plate, parallel to each other and about 1 cm apart.

### TABLE I

#### REAGENT SOLUTIONS

Reagent	Solution	Treatment after spraying with the reagent			
Dithiooxamide	Satd. soln. in 96% ethanol	In NH <sub>3</sub> atmosphere			
Oxine	1% soln. in 80% ethanol	In NH <sub>3</sub> atmosphere, then examine in U.V. light (main- tain NH <sub>3</sub> atm.)			
Dithizone	0.025% soln. in 80% acetone	In NH <sub>3</sub> atmosphere			
Alizarin	Satd. soln. in 96% ethanol	In NH <sub>3</sub> atmosphere; then spray with boric acid soln.			
Boric acid	Satd. soln. in water	spray with some and some			
HNO <sub>3</sub> -glycerol <sup>10</sup>	1% conc. HNO3 and 5% glycerol in 96% ethanol	Dry, then spray with an ammoniacal soln. of Ag <sup>+</sup> , place in U.V. light during 20 min			
o-Tolidine*	0.2% so n. in 10% acetic acid				
Rhodizonic acid	Freshly prepared 0.2% soln. of the Na salt in water				
K ferrocyanide	2% soln. in water				
Morin	1 part of a 1% soln. in 96% ethanol is mixed with 4 parts of conc. HCl	Observe in U.V. light			
Dithiol	0.2 g is discolved in 100 ml of a 1% aqueous soln. of $Na_2CO_3$ by occasional shaking during some hours. The soln. is stabilized by adding so much thioglycolic acid that an opalescence appears	Spray with 2 N hydrochlo- ric acid; then in $NH_3$ atmos- phere			
Chloranilic acid**	0.1% soln. in ether	Observe in U.V. light			
K iodide	5% soln. in water				
Titan yellow	Satd. soln. in water	Dip in 0.5 N NaOH and			
Diphenylcarbazide*	1% soln. in 96% ethanol, add 1 drop of 1 N $H_2SO_4$	spray again with the reagen			

\* Before applying the reagent oxidize by the following procedure: spray with 4 N NaOH, bring the strip in bromine vapour, destroy the remaining bromine in NH<sub>3</sub> atmosphere. Some speed is required.

\*\* For this reagent a dip technique was used<sup>11</sup>: the strip was dipped in the ethereal solution of the reagent, then washed with fresh ether.

(b) Application of the sample solution. A piece of white sewing yarn (e.g. Brook's patent glacé thread No. 60, 0.15 mm thick) of sufficient length was soaked for at least 5 min in a few drops of the sample solution, wiped lightly with a piece of filter paper and placed across the paper strips at a distance of approximately 30 cm from the anode. Care was taken to draw the thread taut. Strips and thread were covered with the upper glass plate, which pressed them together. After 10 min the thread was removed, its position on the strips was marked with a short pencil line and the upper glass plate, fitted beforehand with cellophane membranes and agar gel, was again put into position.

RELATIVE MOBILITIES WITH RESPECT TO THE CO2+-ION, COLOUR

Account multiplication         OWE         NH2         NH2         NH2         NH3         NH4         NH4	Banant and madine		Dithio- Ox		xine Dithizone		Alizarin		Glycerol	Oxidation
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		ir ana meatum:	NH <sub>3</sub>	NH <sub>3</sub>	$NH_3 U.V.$		NH <sub>3</sub>	Boric acid	$AgNO_3 U.V.$	then 🕬 o-tolidine
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Ion		C S	C S	C S	C S	C S	C S	C S	c s
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	T1+	179 ± 1	Ь 15	b 5	d 5	V 10				bl 15
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$Ba^{2+}$	120 ± 3			yf 16					·
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Sr <sup>2+</sup>	119 ± 2			yf 8					
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Ca <sup>2+</sup>	119 ± 2	<u></u>		yf 4		<b></b>			·
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$Mg^{2+}$	118 ± 1		у 1.8	yf 0.9					
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$Mn^{2+}$			У 7	d 2.5		V I.I	V 10	b 0.9	bl 6
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$Fe^{2+}$	107 ± 1			d I		bl o.3	V I	gr† 0.4	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Cr <sup>3+</sup>									bl <b>5</b>
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Co <sup>2+</sup>	100	by 0.8	by 3	dı	V 0.2	v 0.3	V 5		
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Cd <sup>2+</sup>	96 ± 2			yf 2	o o.8				
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Zn <sup>2+</sup>			-	yf 1	rv 0.5	V 3	v 5		
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$Be^{2+}$				•		-			
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$Ni^{2+}$	$85 \pm 5$	v 0.9	у 10	d 2.5	v 0.8	rv 10	rv 10	<del></del>	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Pb <sup>2+</sup>		d 4	у 3		rv 0.7	bl 2	V 2		bl 4
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Cu <sup>2+</sup>		g ı	у 3	d 3	gr 0.5	ı v	v 0.5		
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	La <sup>3+</sup>	45 ± 2		у 3	yf 2.3		bl 3	¥ 3		
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$				-						bl 5
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$			<u></u>						<del></del>	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$				-						
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$				-			rv 1.6			
Ag+ $6 \pm 1$ b $0.5$ $y$ $2$ $yf$ $v$ $1$ $  d$ $0.8$ $-$ Ga <sup>3+</sup> $2 \pm 1$ $ y$ $3$ $yf$ $3$ $ rv$ $rv$ $rv$ $1$ $   -$				by 2			•			
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$				y 30	•	0 1.5	rv 1.4	o 1.7		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$			b 0.5	y 2	•	V I	÷	******	d 0.8	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$							rv 1	rv I	<u> </u>	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	VO <sup>2+</sup>	2 <u>±</u> 1		y 2.5	d 2		οı	r I	đ 1	bl <b>3</b>
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Hg <sup>2+</sup>	O		У7	d 5	o o.8		<b>v</b> 6	<del></del>	
$Bi^{3+}$ $-9 \pm 3$ b       I.4       y       I.4       yft 1.4       o       o.5       v       o.6       v       o.6       -		0		<u></u>		<del></del>			by 2	
$Bi^{3+}$ $-9 \pm 3$ b       I.4       y       I.4       yft 1.4       o       o.5       v       o.6       v       o.6       -		$-9 \pm 2$	<u> </u>	y 10	d 2		v 6	rv 2		
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$			b 1.4	у 1.4		0 0.5	v 0,6	v 0.6	·	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$				gr 1	d 1		v 3	v 7	b 1.1	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$									b 2	·
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		—26 ± 2	b 15	у 10	yf†† 10		V 10	rv 10	d 7	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	CrO4 <sup>2-</sup>	$-28 \pm 1$		у 10	d 10		rv 10	rv 4	<u> </u>	g† 0.9
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Au <sup>3+</sup>	42 ± 2	b 15	gr 20	d 20	g 20	rv 20	V 10	b 2	g† 3
Ti <sup>4+</sup> $-45 \pm 3$ $y$ 10       yf $y$ $v$	Sn4+			y 2	yf 2		02	02		
$Zr^{4+}$ -52 ± 2 - y 8 yf 5.5 - rv 5 rv 6	Ti <sup>4+</sup>			у 10			V 10	rv 5		
	Zr <sup>4+</sup>			-			rv 5			
	$MoO_4^{2-}$	—57 ± 2		у го	d 10					

\* Appearing after some time; † appears at once; \*\* disappears within a short time, except when the concentration of the ion is high; †† in higher concentrations: d.

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## reactions (c) of the ions and their sensitivity (s) (mg/ml)

Rhodizonic	K ferro-	Hydrogen sulphide		Morin	Dithiol		Chloranilic	
acid	cyanide .	Citric acid	NH <sub>a</sub>	<i>U.V.</i>	2N HCl	NHa	acid	Special reagents
C S	C S	C S	C S	C S	C S	C S	C S	
							gr 9	KI: y 15
r** 3							••	
r** 10							by 35	
		<del></del>					y 16	
**				—			y 20	Titan yellow: 0 15
**	bl 1.7	 _1		*****		 1	у 10	
	DI 1.7	d I	d ı		gr 3	br 1	gr 3	Dinhenvloarhaaida
						—		Diphenylcarbazide r 5
			d 0.8		gr 1	gr 1		
** * *		У7	У7				v 3	
						<del></del>	·····	
	·······					**************************************	V IO	
			gr 3	<del></del>	gr 3.5	gr 3.5		
rv 0.7 b 2	 1	gr2 b6	gr 2		у 3		b .4	
**	ьз	0 0	<b>Ь</b> б		gr 5	gr 5	V 10	
o** 3							у 9	
				<u></u>	********	<del></del>	у 11	
							*** 3	
0** 4				yf 10			rv 3	
o** 2.5	b 2.5			yr 10			у 15 0 2.5	
r** 5					r 10		v 30	
		d 0.8	d 0.8		у 3	у 3		
			<u> </u>	yfı	·····	····	v 3	
r** 5			<u> </u>			******	gr 3	
**	g* 5	b 10	b 10					
		y 2.5	y 2.5					AgNO <sub>3</sub> : y 10
				yf 15		<del></del>		
rv** 0.6		b 0.6	b 0.6		O I.7	o 1.7		KI: y 0.4
**	bl o.g	gr 2 *	gr 2		gr 1	gr 1	gr 3	
	<del></del>						<u></u>	AgNO <sub>3</sub> : y 10
		у 10	у 10	yf 15	у 10		<del></del>	
	<u></u>							Diphenylcarbazido r 5
	g 7	b 7	b 7	•	p 10	b io	gr 7	
 •				••••	r 2			
				yf 10				
				<b>yf</b> 6*				
A SARAH		·	<del></del> .		g 3	g 3	V 10	

Abbreviations used: bl = blue; by = brown-yellow; g = green; o = orange; rv = red-violet; yf = yellowfluorescence; b = brown; d = dark, black; gr = grey; r = red; y = yellow; v = violet. Finally the electrodes were clamped on and the plates were loaded with the iron blocks. (c) Electromigration and detection. A voltage of approximately 30 V/cm was applied across the strips, for one hour, after which the position of the various ions was determined.

(d) Determination of the relative mobilities. The relative mobilities, defined by:

distance travelled by ion 
$$X \times 100$$

relative mobility of ion  $X = \frac{1}{\text{distance travelled by the Co}^{2+} \text{ ion on the same strip}}$ 

were evaluated from experiments with solutions of each of the ions together with the Co<sup>2+</sup> ion.

(e) Sensitivity determinations. Decreasing concentrations of each of the ions studied were examined by the technique described above to determine the limits of detection.

#### RESULTS

The relative mobilities of several of the ions mentioned in the first section of this paper. together with standard deviations, are given in Table II. Their colour reactions with the developing reagents and the sensitivities of these reactions, are also given. INcitric acid cannot be used as a medium for those ions listed in Table III, for the reasons stated.

TABLE III

IONS THAT ARE DIFFICULT TO DEAL WITH IN THE CITRIC ACID MEDIUM

Species	Reason	Other supporting electrolytes permitting a separation			
K+	Detection with chloranilic acid, follow-				
Na <sup>+</sup>	ing the procedure of BARRETO AND	0.1 $M$ (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> <sup>3, 5, 12</sup> ;			
Li <sup>+</sup> )	BARRETO <sup>11</sup> gave negative results	0.75 $M$ formic acid <sup>3</sup>			
Cl-	Is transferred to the agar gel around the anode under the conditions described	2% (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> <sup>4</sup>			
MnO <sub>4</sub> -	Not stable in the medium	$M (NH_4)_2 CO_3$			
$SeO_3^{\tilde{2}-}$	Too small differences in mobility	$ScO_3^{2-}$ and $TeO_3^{2-}$ in 2%			
SeO <sup>32-</sup>		$(NH_4)_2CO_3$ <sup>4</sup> ; all three in 0.4 N			
$TeO_3^{*2}-$		$Na_3SO_4$ or 0.1 N $H_3SO_4^{13}$			
$WO_4^{32-}$	Is not easily detected in the $I N$ citric acid medium	0.1 $M$ lactic acid <sup>14</sup> ; 1 $M$ (NH <sub>4</sub> ) <sub>2</sub> CC			

### APPLICATION OF THE METHOD IN QUALITATIVE ANALYSIS

A solution of the sample in I N citric acid is prepared. In the case of Bi<sup>3+</sup> and Sb<sup>3+</sup> where it is impossible to obtain such a solution due to hydrolysis, hydrochloric acid is added to the sample until a clear solution is obtained. Small amounts of HCl do not affect the results, but excess should be avoided.

The presence or absence of the  $Co^{2+}$  ion is established in a preliminary experiment. Electromigration for 15 min is sufficient to identify the ion as a vellowbrown zone after spraying the strip with dithiooxamide and neutralizing in an atmosphere of  $NH_3$ . If the result is negative or dubious, a  $Co(NO_3)_2$  solution in I N

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citric acid is added to the sample mixture, such that the concentration of  $Co^{2+}$  is approximately 5 g/l. Analysis of this solution is carried out as described above.

The position of the  $Co^{2+}$  ion (which travels about 20 cm), is determined by spraying one strip with dithioöxamide solution; the position of some other ions is also revealed by this reagent. Another strip is sprayed with oxine solution and examined. In general, many ions can be identified from the relative mobilities with respect to  $Co^{2+}$ ; this is occasionally aided by characteristic colours or fluorescence of the oxinates. Confirmation is obtained by applying the other reagents mentioned in Table II to the remaining strips, preferably in the order given. If then the  $Co^{+2}$  ion is not found again, an additional spray with dithiooxamide, *e.g.* on the back of the paper; can be helpful.

### DISCUSSION

One advantage of the procedure is that there is no perceptible electro-endosmosis; another one is that diffusion of products of electrolysis to the working zone is inhibited by the agar gel and the cellophane.

Because of the capillary action of the half-wet paper, we used the threadtechnique described above (by which the initial zone width is only 2-3 mm), instead of the common methods with pipets, etc., which give unduly wide zones. In control experiments, spectrophotometric and titrimetric measurements showed that the quantity of solute transferred to the paper amounts to the portion present in 2.5-4 cm thread length, though only 2 cm is in actual contact with the paper. A disadvantage is that differences in diffusion velocities give rise to alterations in the ratios of the concentrations of the ions during their transport to the paper, *e.g.*, in the original solution the ratio of Fe<sup>3+</sup>:Ag<sup>+</sup> and Fe<sup>3+</sup>:PO<sub>4</sub><sup>3-</sup> was I:I but on the paper the former was I:I.5 and the latter was I:I.I. Finally it was found that the amount of solute transferred is hardly influenced either by variation of the humidity of thread and paper, the time of contact or the pressure applied to the thread.

In spite of the precautions taken, the humidity of the paper cannot be fully controlled and the ions will not cover strictly equal distances in the various paper strips. Therefore the use of the  $Co^{2+}$  ion as a reference standard for each strip appeared to be inevitable. The  $Co^{2+}$  ion has been chosen as a standard because it moves rather quickly and is easily detected. However, this introduces the necessity of a preliminary experiment to determine the presence of  $Co^{2+}$  in the mixture.

For reproducible results, the electromigration time should be kept roughly constant.

Most of the anions show only small differences in mobility and give rise to broad zones. This combined with the fact that anions are not easily detected, makes their analysis rather difficult. Though these objections are not fully eliminated it is better to avoid the possible disturbing action of the citric acid and use  $(NH_4)_2CO_3$  as supporting electrolyte, a method described by LEDERER<sup>4</sup>. We recommend this electrolyte also for alkali metals<sup>3, 5</sup>. Other groups that cannot be separated or distinguished by the method described are  $Al^{3+}-Y^{3+}$ , lanthanides, and  $Sr^{2+}-Ba^{2+}$ .

Though no relative mobilities are reported by EVANS AND STRAIN<sup>6</sup> and by MUKERJEE<sup>7</sup>, the sequence in their experiments with restricted groups of ions is in general the same as the one reported here for the same supporting electrolyte. LEDERER<sup>8</sup> found a somewhat different sequence in 1 % citric acid.

As may be concluded from Table II the sensitivity of the method is not very high for some ions, eg. the alkaline earth metals. This can be explained by the fact that the sample solution is diluted during the diffusion from the thread and the subsequent electromigration. Also there will be competition between the complex formed by the ions with the citric acid and the developing reagents. However, many ions can be detected in concentrations ranging from 1:100 to 1:1000 (w/v), and an experienced analytical chemist may be able to detect even lower concentrations.

The oxidation reaction before application of *o*-tolidine should be performed quickly but carefully; too heavy spraying with 4N NaOH and too prolenged treatment with bromine weaken the paper. This reaction for  $Cr^{3+}$  is not always reliable as the zones of  $Cr^{3+}$  and  $Co^{2+}$  coincide, and the presence of a reagent, used for the detection of the latter, interferes with the identification of the former. For this reason no definite value for the relative mobility of  $Cr^{3+}$  can be given. It is advisable to oxidise the  $Cr^{3+}$  to  $CrO_4^{2-}$  before the electromigration. The citric acid does not perceptibly reduce this ion during the experiment, even at a hydrochloric acid concentration of 2N, except in the presence of  $Mn^{2+}$  or  $Ce^{3+}$ .

The excess of acid necessary to keep some ions (Bi<sup>3+</sup>, Sb<sup>3+</sup>, Sn<sup>4+</sup> and Ti<sup>4+</sup>) in solution does not affect the relative mobilities of the cations. The mobilities of the anions are slightly lower because of the initially high ionic concentration and thus lower field strength in the anodically moving zones (see also EDWARD<sup>9</sup>). However, Au<sup>3+</sup>, moving principally as the chloroaurate (III) ion (as concluded from the appearance of chloride in the zone after precipitation of the metal), is 10 % faster in the presence of 2N hydrochloric acid. The effect of hydrochloric acid on Fe<sup>3+</sup> is more serious though; in 2N acid the relative mobility was nearly twice the original value. The sensibility to small local differences in hydrochloric acid concentration may be the cause of the corrugated appearance and trailing of the Fe<sup>3+</sup> zone, and if Fe<sup>3+</sup> and Au<sup>3+</sup> are present together with hydrochloric acid interference with the detection of some of the faster moving ions could occur.

In conclusion, the composition of a sample, containing a mixture of ions can be determined by the above technique within a short time. The method has been incorporated in the students curriculum in this laboratory.

## ACKNOWLEDGEMENTS

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## SUMMARY

A method for qualitative analysis of mixtures of inorganic ions by paper electromigration in I N citric acid at 30 V/cm is described. A thread technique for the application of the sample is described, which gives narrow initial zones. Thirty-eight ions are characterized by their relative mobilities with respect to the Co<sup>2+</sup> ion and their colour reactions with spray reagents; the sensitivities have also been determined. Analysis of mixtures by this technique is satisfactory and rapid.

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