LETTERS TO THE EDITORS

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Inorganic Paper Chromatography

PROF. R. P. LINSTEAD kindly sent me a manuscript copy of the communication by Burstall, Davies, Linstead and Wells[1], and I should like to comment on this work in relation to my own.

Prof. Linstead and his colleagues mention that more precise separations were achieved by them by downward development; this technique was tried by me[3], but more constant R_f values are obtained by Williams and Kirby's method[4].

It is mentioned[1] that separations of gold, platinum, palladium, iridium and rhodium have been carried out by the authors. I have since devoted some more time to the platinum metals, including ruthenium and osmium, and intend to publish my results in the near future.

My results on the separation of the copper and tin groups were accepted by *Analytica Chimica Acta* on September 24, 1948, in advance of Arden, Burstall, Davies, Lewis and Linstead's first publication[2], and is at present in the press.

More recent work of mine includes the following. Silver chloride, mercurous chloride and lead chloride can be separated on a disk of filter paper by placing approximately 0·1 mgm. in the centre and adding two drops of water followed by two drops of 5*N* ammonium hydroxide as developing solvent. After exposure to hydrogen sulphide, this produces a centre patch of black mercury and mercury sulphide surrounded by a ring of silver sulphide, again surrounded by a ring of lead sulphide.

Divalent copper and cadmium can be separated by the technique described in ref. 3 by the use of 25 per cent ethyl alcohol as developer.

Divalent lead can be separated from divalent copper, cadmium and mercury, and trivalent bismuth by development with 1*N* aqueous hydrochloric acid; but the lead does not travel with the liquid front.

Using butanol saturated with 1*N* hydrochloric acid, the following R_f values were obtained:

Ion	R_f value	Ion	R_f value
Ag+	0·0	Hg++	1·02–1·10
Cu++	0·08–0·13	Pt+++	0·72–0·8
Cd++	0·56–0·65	Rh+++	0·07
Bi+++	0·61–0·68	$RuO_4^=$	0·1
Pb++	0·0	Ir++++	0·72–0·8*
As+++	0·67–0·73	Au+++	1·05–1·13
Sb+++	approx. 0·8*	Fe+++	0·12
Sn++	0·95–0·99	Co++	0·07
$MoO_4^=$	0·5–0·53	Ni++	0·07
UO_2++	0·2	Mn++	0·09
U++++	0·0	Sr++	0·0
Pd++	0·6	Ba++	0·0

* Further details are necessary.

Investigations with other solvents were also carried out; for example, hydrobromic, hydriodic, acetic, nitric and phosphoric acids, in butanol, etc.

On January 25, 1949, I submitted a paper to *Science* giving the details of the separation of chloride, bromide, iodide and thiocyanate ions, which is achieved by using butanol saturated with 2*N*; the following R_f values were obtained:

Anion	R_f value
Cl−	0·10–0·11
Br−	0·15–0·18
I−	0·29–0·32
CNS−	0·42–0·48

For separation of smaller quantities a new technique, which I call micro-chromatography, was developed and announced to some of my colleagues in this field on December 31, 1948, in a private communication. Further details will appear in due course.

The above deals only with inorganic work. In addition, I have dealt with a number of theoretical points, including: a thermodynamical treatment of temperature variations; new aspects of 'comet' formation; generalizations concerning the effect of different anions on the R_f values of cations.

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[1] [See *Nature*, January 8, p. 64.]
[2] Arden, Burstall, Davies, Lewis and Linstead, *Nature*, **162**, 691 (1948).
[3] Lederer, M., *Analytica Chimica Acta*, **2**, 261 (1948), received by the editors on March 20, 1948.
[4] Williams, R. J., and Kirby, H., *Science*, **107**, 481 (1948).

THE spread of interest in inorganic adsorption analysis using organic solvents, indicated in Mr. Lederer's communication above and in the recent letter from Pollard, McOmie and Elbeih[1], is welcome, as it does seem that the method will have wide applications. We have tried to make its possibilities generally known both in our preliminary communications[2], by demonstrations[3], and by privately advising a number of research laboratories on applications to their individual problems.

The further development of this method may proceed along many different lines. One possibility is to compare the behaviour of a large number of different metals with standard solvents or solvent mixtures. This could conceivably lead to the separation of complex mixtures of metals in two-dimensional chromatograms, rather as has been done with amino-acids. It is interesting that both Mr. Lederer and the Bristol workers are collecting comparative data suitable for this purpose. It is, of course, necessary to bear in mind that the rate of movement of a particular metal (as represented, for example, by its R_f value) may be affected by other ions present. Another line of attack is to devise special methods for particular and more limited mixtures. Thus a group of metals can be precipitated in some standard way, and paper chromatography used as a supplementary weapon for analysis or purification. This is a line of development which we think very attractive, and one topic which we are now studying particularly is the possibility of eluting one metal after another from a paper strip or column by successive changes of the extracting medium. Separations involving some forty-five metals and anions have so far been achieved in this Laboratory. Details will appear elsewhere.

In view of the increasing interest in this subject it may be well at this stage to make a few historical matters clear. The separation of organic substances from aqueous solutions by capillary analysis was first due to Goppelsroeder[4], while it appears that H. Trey[5] achieved the first clear inorganic separations by this technique. The fractionation of inorganic compounds in aqueous solutions by means of adsorption columns was first effected by Schwab and his co-workers[6]. The great advance of the separation of *organic* compounds on paper using organic solvents was due to Martin, Gordon, Synge and their collaborators[7]. We appear to have been the first to have described the use of *organic* solvents for separating *inorganic* materials on cellulose, although it now