

CHROMATOGRAPHY ON PAPER IMPREGNATED WITH INORGANIC ION EXCHANGERS

IV. SPOT TEST FOR Tl(I), Hg(I), Ag(I) AND Cs(I) AFTER RAPID AND SELECTIVE CHROMATOGRAPHIC SEPARATION ON AMMONIUM MOLYBDOPHOSPHATE PAPER*

G. ALBERTI

Laboratorio di Chimica delle Radiazioni e Chimica Nucleare del C.N.E.N., Istituto di Chimica Generale ed Inorganica dell'Università di Roma, Rome (Italy)

(Received June 30th, 1967)

Spot test reactions on paper can be employed for the fast qualitative detection of very small amounts of inorganic ions¹. It is often very difficult, however, to find highly specific reagents for a given ion. Therefore even the qualitative results of spot test reactions become doubtful if interfering substances are present and previous separations become necessary. It is clear that utilization of spot test reactions on paper can be increased considerably if a rapid and selective separation from the interfering substances can be accomplished directly on the paper itself, *e.g.* by a short ascending chromatography. In this case a given ion could be recognized, both by a specific spot test reaction and by the characteristic R_F value. For such a purpose chromatography on ion exchange paper seems to be particularly attractive, especially when the ion exchanger employed shows a high selectivity only for a few inorganic ions. Since ammonium molybdophosphate (AMP) is very selective ion exchange material for cations of large ionic radius² such as Tl(I), Ag(I), Hg(I) and Cs(I), the possibility of employing AMP paper for very fast chromatographic separation of these ions followed by spot test reactions has been examined. For such a purpose the chromatographic behaviour of numerous inorganic cations on AMP paper has been investigated.

EXPERIMENTAL

Analytical procedure

Erba RP products were used without further purification. Cu, Tl, Ag, Hg, Ni, Fe, Co, Pb, Sb and Bi were detected as sulphides; Cs, Rb, Na and Sr were detected radiometrically using ¹³⁴Cs, ⁸⁶Rb, ²²Na and ⁸⁹Sr as tracers. Li and K were detected by flame photometry while U and Eu were detected by their fluorescence as described in a previous paper³. Other ions were detected by the usual spot test reactions¹.

Preparation of AMP-impregnated strips or discs

AMP-impregnated strips were prepared as described in a previous paper⁴.

* This work has been supported by the "Consiglio Nazionale delle Ricerche".

Paper discs with a small spot of AMP in the centre were prepared in the following manner: 0.01 ml of a solution obtained by dissolving 6 g of AMP (Bio Rad Laboratories) in 25 ml of 4 *N* ammonia solution were spotted on the center of a disc of Whatman No. 1 paper. The disc was dipped for 10 min in a solution containing 25 g ammonium paramolybdate, 104 ml 65 % nitric acid and 638 ml distilled water. It was washed first in a solution of 1 *N* ammonium nitrate and then twice in distilled water.

Chromatographic results

In Table I the chromatographic behavior of a large number of inorganic cations on AMP paper is reported. A solution which was 7.4 *M* in NH_4NO_3 and 1 *M* in HNO_3 was employed as eluent. It can be noted that only Cs(I) and Tl(I) are strongly retained by AMP under these conditions; AMP paper can thus be employed with success for the selective separations of Cs(I) and Tl(I) ions from all cations examined and probably from many others.

Table II shows the chromatographic behaviour of Cs(I), Tl(I), Hg(I) and Ag(I) when eluted with 1 *M* HNO_3 at various concentrations of NH_4NO_3 . It can be seen that the separation Cs(I)-Tl(I) is improved at a high NH_4NO_3 concentration while the opposite occurs for the Hg(I)-Ag(I) separation.

TABLE I

CHROMATOGRAPHIC BEHAVIOUR OF SOME INORGANIC IONS ON AMP PAPER

Eluent: 7.4 *M* NH_4NO_3 in 1 *M* HNO_3 .

<i>R_F</i> range	Ion
0 - 0.15	Cs(I)
0.15-0.25	Tl(I)
0.25-0.70	—
0.70-0.80	Hg(I); Ag(I); Rb(I)
0.80-1	Al(III); Ba(II); Be(II); Bi(III); Cd(II); Ce(III); Ce(IV); Ca(II); Co(II); Cr(III); Cu(I); Cu(II); Dy(III); Eu(III); Fe(II); Fe(III); Ga(III); Gd(III); Hg(II); K(I); La(III); Li(I); Lu(III); Mg(II); Mn(II); Mo(VI); Na(I); Nd(III); Ni(II); Pb(II); Pd(II); Sb(III); Sm(III); Sn(II); Sn(IV); Sr(II); Tb(III); Te(IV); Th(IV); Ti(III); Tl(III); UO_2 (II); V(V); Y(III); Zn(II); Zr(IV)

TABLE II

R_F VALUES OF Cs(I), Tl(I), Hg(I) AND Ag(I) ON AMP PAPEREluent: NH_4NO_3 at various concentrations in 1 *M* HNO_3 .

Ion	NH_4NO_3 molarity						
	0.1	0.5	1	3	5	7.4	15
Cs	0.0	0.0	0.0	0.10	0.10	0.13	0.23
Tl	0.0	0.0	0.02	0.06	0.13	0.20	0.40
Hg	0.15	0.40	0.41	0.58	0.68	0.75	0.81
Ag	0.46	0.63	0.65	0.73	0.74	0.76	0.86

TABLE III

CHROMATOGRAPHIC BEHAVIOUR OF SOME INORGANIC IONS ON AMP PAPER

Eluent: 0.5 M NH₄NO₃ in 1 M HNO₃.

<i>R_F</i> range	Ion
0 - 0.05	Cs(I); Tl(I)
0.05-0.40	—
0.40-0.45	Hg(I)
0.45-0.60	—
0.60-0.65	Ag(I)
0.65-0.75	Au(III)
0.75-1	Ba(II); Ca(II); Cd(II); Ce(III); Co(II); Cr(III); Cu(II); Dy(III); Eu(III); Fe(III); Gd(III); Hg(II); La(III); Li(I); Mg(II); Na(I); Ni(II); Pb(II); Th(IV)

Table III shows the chromatographic behaviour of some ions when developed with 0.5 M NH₄NO₃ solution in 1 M HNO₃. Also in this case the concentration of NH₄NO₃ is high enough to displace most of the ions examined to the front or near it; furthermore a sharp separation of Tl(I), Ag(I), Hg(I) can be obtained.

Spot test determination of Tl(I) on filter paper and AMP paper

In concentrated solutions of chlorides, Tl(I) gives a strong fluorescence ($\lambda_e = 247 \text{ m}\mu$; $\lambda_f = 475 \text{ m}\mu$) due, according to MAKISHIMA *et al.*⁵, to the formation of the chlorocomplex TlCl₃⁻. The fluorescence of this complex can be utilized to detect Tl(I) on filter paper. For this purpose a drop of the solution to be examined is spotted on the filter paper, then a concentrated solution of CaCl₂ is sprayed on it. After drying the filter paper by a current of hot air a blue fluorescent spot can be observed under U.V. light if Tl(I) is present (identification limit 0.2 μg ; dilution limit 1:10⁴). If an analogous procedure is carried out on AMP paper a yellow-green fluorescence is observed*.

As the selectivity of AMP for Tl(I) is very high, it is possible to obtain concentrated spots of Tl(I) from dilute solutions of Tl(I). For such a purpose the tip of a micropipette containing the Tl(I) solution is put on the AMP paper and a relatively large volume of this solution (10⁻² to 10⁻¹ ml) is allowed to be slowly absorbed by the paper. Tl(I) is thus concentrated in a very narrow zone and the dilution limit of Tl(I) can be lowered to 1:10⁶. However, on AMP paper Tl(I) is partially oxidized to Tl(III) in the presence of chloride ions; a dark-blue spot is thus formed due to a reduction product of AMP. This reaction is very similar to that of Tl(I) with phosphomolybdic acid and hydrobromic acid⁶ and can be utilized to detect Tl(I) if no other reducing ions are present.

Many inorganic ions may quench the fluorescence of Tl(I) or may reduce AMP giving dark spots. In Table IV the per cent of quenching caused by 100 μg of some inorganic ions on 50 μg of Tl(I) is reported. Some strong reducing ions giving dark spots are also reported in this table.

* Tl(I) fluorescence on AMP paper is enhanced if nitrate ions are present.

TABLE IV

PERCENT QUENCHING BY 100 μg OF VARIOUS IONS ON THE FLUORESCENCE OF 50 μg OF Tl(I)

Quenching (%)	
0- 10	Li(I); Na(I); K(I); Rb(I); Cs(I); Ag(I)
10- 50	Ca(II); Sr(II); Ba(II)
50- 80	Hg(II); Ni(II); Co(II)
80-100	Fe(III); Cr(III); Tl(III); Cu(I)*; Sn(II)*; Fe(II)*

* Dark-blue spots, due to reduction of AMP, are formed.

These data show that even low concentrations of interfering substances interfere strongly; however, as already shown, Tl(I) can be easily separated from all examined interfering substances by chromatography on AMP paper. The spot test procedure using AMP discs can be carried out as follows: the tip of a micropipette containing the solution to be examined is put in the center of the AMP spot and $2 \cdot 10^{-3}$ to 10^{-2} ml of solution are allowed to be adsorbed by the paper. To separate Tl(I) from interfering substances the tip of a capillary containing a 0.5 M NH_4NO_3 -1 M HNO_3 solution is then put at the center of the AMP spot until about 0.1 ml of this solution is absorbed by the paper*. Then the tip of another capillary containing a 8 M CaCl_2 solution is placed on the AMP spot until about 0.1 ml of this solution is absorbed. A dark spot is formed if Tl(I) is present. Under U.V. a yellow-green fluorescence is observed. When ions giving insoluble chlorides are not present in the solution to be examined, the test described can be further simplified by eluting the interfering substances directly by an NH_4NO_3 solution containing Cl^- ions. It was found that a solution 3 M in NH_4NO_3 , 5 M in NH_4Cl and 4 M in CaCl_2 gives satisfactory results. The test can be carried out in a very short time (less than 60 sec) and has been employed with success to detect Tl(I) in various complex mixture of inorganic ions. Tl(I), after separation from the interfering substances, could be eluted from AMP paper and determined quantitatively in solution by fluorescence. However, difficulties are encountered in the elution since Tl(I) is strongly retained by AMP. To overcome this difficulty Tl(I) can be oxidized to Tl(III) by a dilute KClO_3 solution in 6 N HCl and, after elution, again reduced to Tl(I) by hydroxylamine in ammonia solution. This procedure however is too long and is difficult to standardize; thus Tl(I) determination on AMP paper gives real advantages over other conventional methods only if rapid qualitative or semiquantitative data are required.

Spot test detection of Hg(I), Ag(I) and Cs(I)

As can be seen from Tables II and III, AMP paper can be employed also for separation of Hg(I), Ag(I) and Cs(I) from interfering substances. In this case too the ions, after chromatographic separation, can be detected by conventional spot test procedures and recognized by their characteristic R_F value on AMP paper. Since AMP paper is very selective towards Cs^+ (Ref. 2), AMP paper can be used to obtain concentrated spots of this ion. For such a purpose the end of a strip of AMP paper is

* Only Cs^+ ion is not well separated from Tl(I) by this procedure. However, this ion, as seen in Table IV, is not an interfering substance of Tl(I) fluorescence.

dipped into the solution containing traces of Cs(I). The Cs ion remains concentrated in a very sharp zone of the AMP paper near the immersed extremity.

SUMMARY

Spot tests for Tl(I), Ag(I), Hg(I) and Cs(I), in the presence of interfering substances, have been carried out after a very fast chromatographic separation on paper impregnated with ammonium molybdophosphate. The time required, in some cases, is less than 60 sec. The chromatographic behaviour of several inorganic ions on AMP paper is also reported.

REFERENCES

- 1 F. FEIGL, *Spot Tests in Inorganic Analysis*, Elsevier, Amsterdam, 1958.
- 2 J. VAN R. SMIT, J. J. JACOBS AND W. ROBB, *J. Inorg. Nucl. Chem.*, 12 (1959) 95, 104.
- 3 G. ALBERTI, M. A. MASSUCCI AND E. TORRACCA, *J. Chromatog.*, 30 (1967) 579.
- 4 G. ALBERTI AND G. GRASSINI, *J. Chromatog.*, 4 (1960) 423.
- 5 S. MAKISHIMA, T. TOMOTSU, M. HIRATA, S. HAYAKAWA, K. HASEGAWA, R. KAMBE AND S. SHIONAYA, in H. P. KALLMANN AND G. M. SPRUCH (Editors), *Luminescence of Organic and Inorganic Materials*, Wiley, New York, 1962, p. 472.
- 6 F. FEIGL, *Spot Tests in Inorganic Analysis*, Elsevier, Amsterdam, 1958, p. 156.

J. Chromatog., 31 (1967) 177-181