

CHLORANILIC ACID AS A REAGENT IN THE PAPER CHROMATOGRAPHY OF INORGANIC COMPOUNDS

II. HEAVIER METALS

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(Received May 14th, 1960)

INTRODUCTION

We have already studied the use of chloranilic acid as a reagent in the paper chromatography of alkali and alkali earth metals¹, with extremely good results. Its application to the identification of chromatographic spots of heavier metals was the next logical step, since BARRETO² had already used it in the determination of zinc and VOIGT³ in that of zirconium.

In order to make a general approach to the subject we took samples from all the remaining analytical groups, and examined their chromatographic behaviour and the sensitivity of chloranilic acid towards each one of them. In the present paper the results of this work are presented.

MATERIALS AND METHODS

Reagent

As in the other instances¹, chloranilic acid was used as a 0.1 % (w/v) solution in ether (kept in a dark bottle in the refrigerator), and the detection of the spots was carried out by dipping the dry paper for a few seconds in the reagent, and afterwards washing it twice with ether. The cations appear as dark spots under U.V. light, or as coloured zones, by daylight, in the case of higher concentrations.

Sample solutions

Samples were prepared by dissolving a sufficient amount of the acetate in water to obtain a solution containing 0.1 % of the cation, or, in some cases, by dissolving a calculated amount of the oxide in glacial acetic acid. These 0.1 % solutions were diluted as required.

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Sensitivity evaluation

The sensitivity was evaluated first by means of a spot-test on filter paper¹ and then by running paper chromatograms with increasing concentrations, starting at the limits formerly established.

Paper chromatography

Macherey-Nagel No. 261 filter paper was used, and the first runs were carried out by the ascending technique, using ERLNMEYER'S⁴ solvent system (96 % ethanol-2 *N* acetic acid, 80:20). Later on, many other solvent systems were investigated, as we wished to find the best means for a two-dimensional separation. Moreover, ERLNMEYER'S solvent gave tailing spots with ferric iron, which disturbed the identification of the other cations.

We had either to obtain a compact Fe³⁺ spot or to eliminate it by elution, and therefore we tried the following solvent systems: acetic acid-methanol⁵, acetone-acetic acid-methyl ethyl ketone (50:10:40), acetone-ethanol-acetic acid (95:4:1), dioxan-water (90:10 and 80:20) and a modification of ALMASSY'S solvent⁶, containing ethanol-acetic acid-ether (17:3:80). The best results, however, were obtained with acetone-8 *N* acetic acid (90:10). In this case the descending technique was used, iron being displaced with the solvent front.

When silver samples were spotted the chromatograms were run in the dark room, in order to avoid reduction.

RESULTS

The results obtained with the described technique are summarized in Table I. Sensitivity was expressed as the minimum amount of the cation (in μg) detectable after chromatographic separation.

TABLE I
SENSITIVITY OF CHLORANILIC ACID TOWARDS SOME OF THE HEAVIER METALS,
SEPARATED BY PAPER CHROMATOGRAPHY WITH
(1) ETHANOL-ACETIC ACID AND WITH (2) ACETONE-ACETIC ACID

Cation	Sensitivity μg	R_F		Colour of spot
		1	2	
Fe ³⁺	0.01	0.08*	1.00	brownish
Ni ²⁺	0.10	0.34	0.07	greenish
Co ²⁺	0.20	0.42	0.07	yellow
Cu ²⁺	0.10	0.27	0.20	light green
Zn ²⁺	5.00	0.78	0.31	greenish
Ag ⁺	4.00	0.37	0.08	brownish red
Cd ²⁺	2.00	0.71	0.20	brownish
Hg ²⁺	5.00	0.00	1.00	brownish
Pb ²⁺	0.10	0.10	0.09	brownish
U ⁴⁺	1.00	0.83	0.86	brownish

* Tailing.

As can be seen, there was a large variation in the sensitivity of chloranilic acid towards the heavier metals. It was extremely high towards ferric iron, where $0.01 \mu\text{g}$ was detectable, and only moderate with respect to zinc, mercury (II) and silver, where $4\text{--}5 \mu\text{g}$ were necessary. The values for the other metals lay between these extremes, $0.1\text{--}0.2 \mu\text{g}$ of nickel, copper (II), lead and cobalt (III) and $1.0\text{--}2.0 \mu\text{g}$ of uranium (as uranyl acetate) and cadmium, being easily identifiable.

The R_F values were determined after 18-h runs (displacement 30 cm). From these a two-dimensional map was drawn (Fig. 1) and then checked by running a

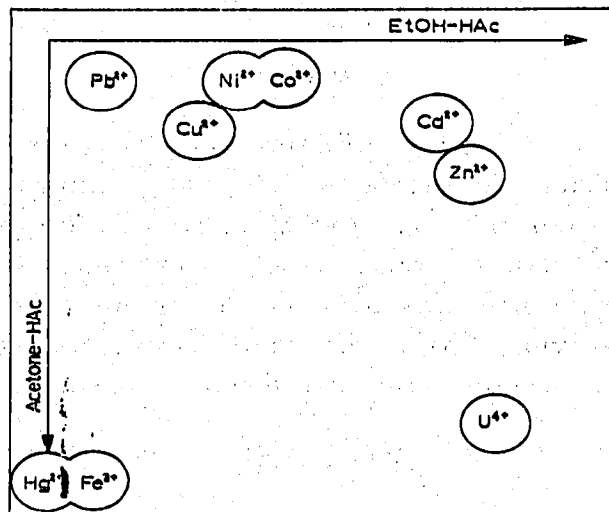


Fig. 1.

chromatogram. The first run was carried out by the descending technique, using acetone-acetic acid, and the second by capillary ascension, with ethanol-acetic acid. Good separations were obtained and well defined spots were found with concentrations that were about five times those considered as the limits of sensitivity (Table I).

DISCUSSION

As has been stated before¹, the main advantages of the use of chloranilic acid as a reagent in the paper chromatography of inorganic compounds are its low specificity and high sensitivity, as well as the short time required for the reaction and the ease with which it can be performed. By using ether as a solvent the risk of eluting material from the spot is completely eliminated, the spot does not diffuse and the chromatogram can be rapidly dried.

The main drawback of the method is that the cations must be run as salts of organic acids (we used acetates), as the reagent seems to be unable to displace the stronger inorganic ones. This limits the choice of the solvent to be used, and excludes HCl-containing mixtures, which are the solvents most frequently applied.

By using acetone-acetic acid for the separation of samples containing iron it is possible to prevent interference from this element, because it is carried to the front

of the solvent (tailing was observed with most of the proposed mixtures). This was specially true in the case of two-dimensional separations, when the first run with this solvent is essential.

ACKNOWLEDGEMENTS

The present work was carried out in the Dept. of Biochemistry of the Central Laboratory of Tuberculosis, with the help of the Institute of Phthiology and Pneumology of the University of Brazil and in collaboration with the Institute of Agricultural Chemistry. One of us (R.C.R.B.) received a grant from the National Council of Research.

SUMMARY

The authors studied the use of chloranilic acid as a reagent in the paper chromatography of some of the heavier metals. Sensitivity was found to vary from 0.01 μg for ferric iron, to 5.0 μg for mercury (II) and zinc. It was found that iron gave tailing spots with most of the solvent systems, which interfered with the separation of the other cations. This interference was avoided by using acetone-acetic acid, which displaces iron to the solvent front. Efficient two-dimensional separations were obtained by carrying out a second run with ethanol-acetic acid.

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