Das beschriebene Verfahren kann auch als Tüpfelreaktion zur Erkennung mancher Beschleuniger Verwendung finden. Die Empfindlichkeit der Reaktion ist hierbei recht verschieden; so lassen sich z.B. 2–5 γ Thiurame und Dithiocarbamate, hingegen 20–50 γ Beschleuniger der übrigen Gruppen sicher nachweisen.

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Separation of Al, Ga, In and Tl by reversed-phase chromatography on papers treated with di-(2-ethylhexyl) orthophosphoric acid

The potentiality and selectivity of reversed-phase partition chromatography with paper treated with di-(2-ethylhexyl) orthophosphoric acid (HDEHP) in inorganic separations has been applied in this laboratory to the rare earths[1] and to the alkali metals and alkaline earths[2,3].

During the systematic study on the chromatographic behaviour of a large number of cations on HDEHP-treated papers, as a function of HCl molarity in the eluent, the possibility of a good separation of Al, Ga, In and Tl became apparent.

Recently, the interest in such elements has considerably increased in connection with new fields of research and technology such as nuclear energy, space communication and semiconductors. It was therefore considered worthwhile to investigate the behaviour of these elements in reversed phase chromatography with HDEHP-treated papers.

The separation of Al, Ga, In and Tl by classical paper chromatography has been attempted by various authors using alcohol–HCl mixtures[4,5,12] or phenol–alcohol–HCl mixtures[6] as eluents.

In the present investigation a good separation of the four elements was obtained on Whatman No. 1 paper pre-treated with 0.1 *M* HDEHP-cyclohexane solutions and eluted with 1 *M* or 8 *M* HCl, these two molarities being selected on the basis of the systematic study referred to above. Preparation of the paper and general procedure are described in a previous work[3]. Chromatography was by the ascending technique at room temperature (23° ± 1°) in tightly closed large jars, with 7 × 46 cm paper strips cut perpendicular to the machine direction.

A stock solution containing $5 \cdot 10^{-6}$ equivalents/ml was prepared for each element and to avoid hydrolysis was brought to different HCl molarities. The molarities of HCl of the respective stock solutions, together with the original substance and Supplier, are as follows: $AlCl_3$ (C. Erba-Milano), 10^{-3} *M* HCl; Ga metal (BDH-London), 0.05 *M* HCl; $InCl_3$ (BDH), $4 \cdot 10^{-3}$ *M* HCl; TlCl (C. Erba), 0.2 *M* HCl. The aluminium and indium solutions were directly prepared by dissolution of the chlorides, that of gallium by HF treatment of the metal and conversion to chloride with HCl, and that of thallium(III) by oxidation of the TlCl solution with *aqua regia*, followed by ether extraction from a 6 *M* HCl solution, precipitation with 0.1 *M* NaOH and final purification, according to the method reported by HORROCKS AND VOIGT[7].

Three spots, about 0.05 ml each, were deposited on every paper strip, one on the central axis of the sheet and the other two equally spaced on either side. The three spots were on a starting line 25 mm from the end of the strip. The central spot contained the four elements and the two lateral ones a group of two or three of the four elements. After elution, the strip was cut longitudinally to obtain three narrow strips. The following procedure was then adopted for the different spots since, for the greatest sensitivity, aluminium and indium are best detected by spraying with a 0.1 % alcoholic morin solution and gallium and thallium with an analogous quercetin solution.

A preliminary check was made for the position of the spots on the two lateral strips, and then the central one was developed with the appropriate solution by spraying the respective positions.

The experimental results obtained by elution of 0.1 *M* HDEHP-treated paper with 1 *M* and 8 *M* HCl are shown in Table I, where the R_F values of the four elements are reported. The R_F values for untreated paper eluted under identical conditions are also reported in this table.

TABLE I

COMPARISON OF R_F VALUES OF Al, In, Tl AND Ga ON TREATED AND UNTREATED PAPER AT DIFFERENT ACIDITIES

Element	R_F			
	1 M HCl eluent		*8 M HCl eluent*	
	HDEHP paper	*Untreated paper*	*HDEHP paper*	*Untreated paper*
Al^{3+}	0.00	0.95	0.78	0.79
In^{3+}	0.32	0.84	0.89	0.90
Tl^{3+} and Tl^{+}	0.78	0.80	0.17	0.74
Ga^{3+}	0.92	0.95	0.04	0.65

From these data, together with the diagrammatic sketch of chromatograms shown in Fig. 1, it appears that a neat separation of the four elements is possible with HDEHP-treated paper and that a separation of In, Tl and Ga is possible on normal cellulose paper, whilst Al gives a spot which is close to that of Tl. The results obtained with untreated paper confirm the trend found by LEDERER AND OSSICINI[8] with Whatman No. 1 paper eluted with HCl, even though their experimental conditions were not exactly the same.

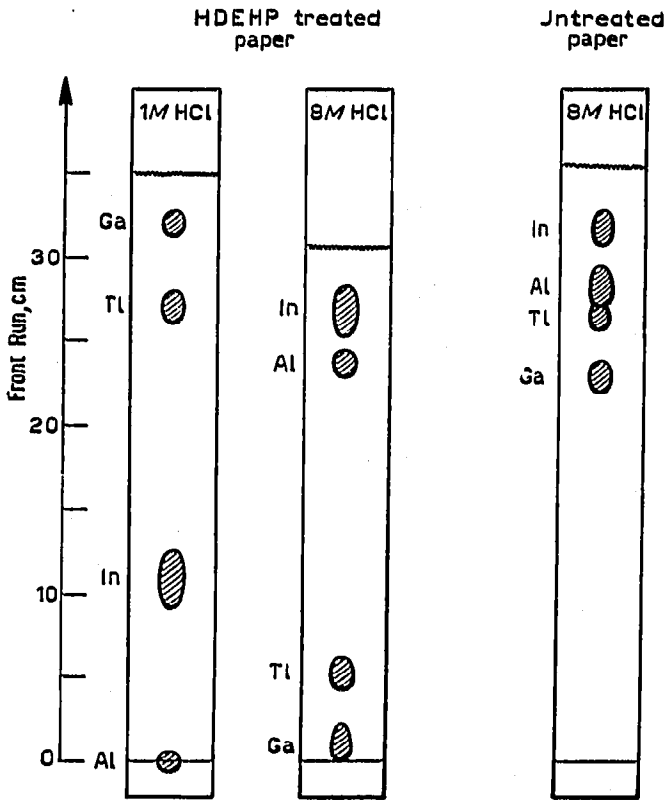

Fig. 1. Diagram of chromatography of Al–Ga–In–Tl on HDEHP-treated paper and on untreated paper.

By comparing the results for HDEHP-paper and untreated paper, with the same eluent, the following conclusions can be drawn:

(i) Aluminium and indium mainly undergo cation exchange with HDEHP. This can be seen from the fact that with 1 *M* HCl they are strongly retained only on the treated paper, whilst with 8 *M* HCl their R_F's are almost identical on both treated and untreated papers;

(ii) The behaviour of thallium and gallium cannot be accounted for by a cation exchange mechanism on HDEHP since at the low acidity they are not adsorbed on HDEHP-paper but are appreciably retained at the high acidity. The formation of anionic chloro-complexes of these two elements, such as $TlCl_4^-$ and $GaCl_4^-$, would suggest an anionic mechanism of adsorption, but this is not likely to occur in the system investigated in this work. On the other hand, experimental evidence exists that such anionic chloro-complexes are strongly adsorbed on cationic resins as Dowex-50[9] and are sensibly retained (low R_F's) by paper treated with a neutral extractant such as tri-*n*-octylphosphine oxide[10].

In Fig. 1 the sequence of elution of the four elements is shown as Ga–Tl–In–Al with 1 *M* HCl and In–Al–Tl–Ga with 8 *M* HCl. In this laboratory, the behaviour of these elements in reversed-phase chromatography on paper and on columns of cellulose powder treated with the same extractant has been shown to be equivalent[11]. Therefore separation of the four elements for purification purposes can be attained with columns made of cellulose powder treated with HDEHP. In the latter case, the possibility of influencing the elution order by altering the acidity of the eluent is a

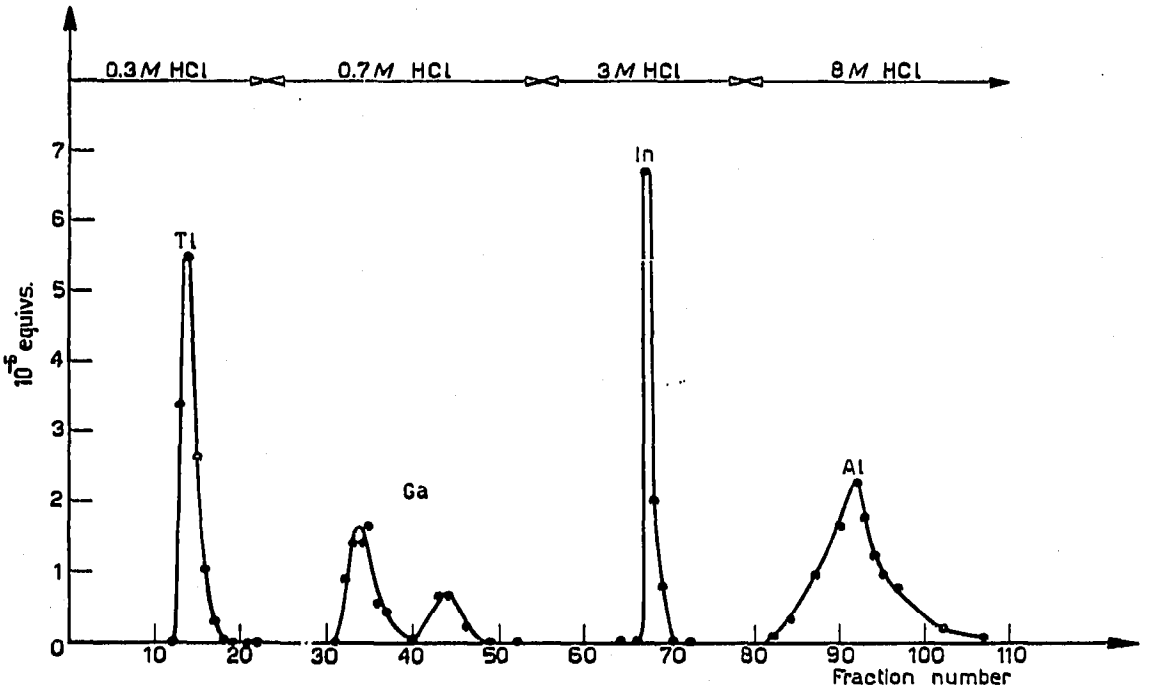

Fig. 2. Separation of Tl–Ga–In–Al (10^{-6} moles each) with HCl on 0.1 *M* HDEHP cellulose powder (bed 13 mm × 250 mm). Fraction volume 2 ml. Flow-rate of eluent 0.5 ml/min.

great advantage, since it is convenient to select conditions whereby the macro-component is eluted from the column whilst the trace impurities are retained.

To check one of the possible applications of the present investigation to column chromatography, a column (13 mm × 250 mm high) was prepared containing cellulose powder (Whatman No. 1) treated with a 0.1 *M* HDEHP–cyclohexane solution. As shown in Fig. 2 the elution order with HCl having different molarities was Tl–Ga–In–Al. A volume of about 1.5 ml of feed solution 0.01 *M* in HCl, containing $5 \cdot 10^{-6}$ moles of each of the elements, was deposited on to the bed which was eluted at room temperature (24 ± 1°) at a flow-rate of 0.5 ml/min.

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