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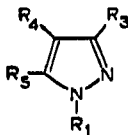
Reversed-phase extraction chromatography using a tetra-substituted pyrazole as stationary phase

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In 1958, Winchester¹ first thought of coupling the favourable features of high-molecular-weight extractants with a chromatographic technique, and reported on the use of di(2-ethylhexyl)phosphoric acid loaded on aluminium oxide for separating a number of rare earths; dilute HCl was used as the mobile phase. Since then, the technique of reversed-phase chromatography, often called reversed-phase extraction chromatography, has become increasingly popular. So far, several hundred papers have been published in this field, most of them dealing with the use of high-molecular-weight amines and substituted quaternary ammonium salts, and of neutral organophosphorus compounds as impregnants of the stationary phase. Solutions of strong monobasic acids are generally used as eluents^{2,3}. Recently, heterocyclic amines, *viz.* 3,4,5-trialkyl- and 1,3,4,5-tetraalkylpyrazoles



have been introduced⁴ as extractants for acids and anionic metal-ligand complexes. In view of the interesting results reported for liquid-liquid extraction systems, the use of two of these extractants in chromatography has now been investigated.

EXPERIMENTAL

Materials

1,3,4,5-Tetraalkylpyrazoles were synthesized by boiling equimolar amounts of the appropriate substituted hydrazine hydrochloride, NaOH and a 2-alkyl-1,3-diketone for 4-5 h in alcohol. After cooling, the product was extracted with chloroform, the organic layer was washed and dried, the chloroform removed and the residue subjected to vacuum distillation. The required 2-alkyl-1,3-diketones were synthesized by acylation of aliphatic acids with the acid chloride in the presence of anhydrous AlCl₃⁵. In the present study, 1-methyl-3,5-dipentyl-4-butylpyrazole (found, C 77.84%, H 12.19%, N 10.04%; calculated, C 77.63%, H 12.31%, N 10.06%) and 1-phenyl-3,5-dipentyl-4-butylpyrazole (found, C 81.16%, H 10.72%, N 8.25%; calculated, C

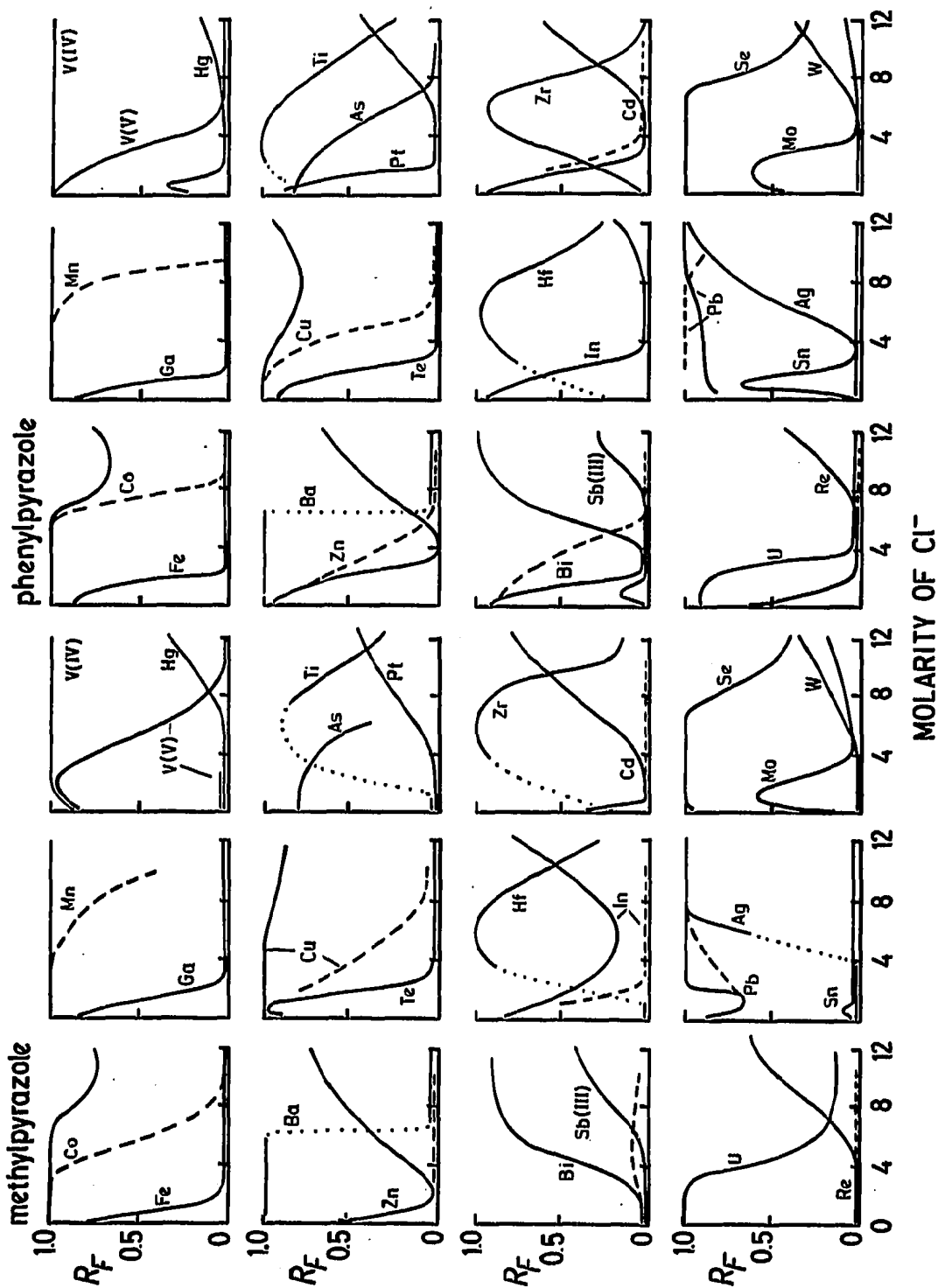


Fig. 1. Plots of R_F versus Cl^- molarity using silica gel impregnated with the methylpyrazole or phenylpyrazole as the stationary phase. Eluents: —, HCl; ---, acidified LiCl. Diffuse spots are indicated by dots.

81.12%, H 10.65%, N 8.23%) were used. They are termed the methylpyrazole and the phenylpyrazole, respectively, in this paper.

Methods

A 0.1 *M* solution of the pyrazole in chloroform was shaken with an equal volume of 2 *N* HCl and thoroughly mixed with silica gel (Type DO, Fluka, Buchs, S.G., Switzerland; SiO₂-CHCl₃ = 1:6, w/v). Chromatoplates were prepared by dipping microscope slides into the resulting suspension. After evaporation of the chloroform, a thin layer of pyrazole-impregnated silica gel adhered to the plate.

The sample solutions contained 1–10 mg/ml of ion and were acidified with HCl as necessary in order to prevent hydrolysis. With the metal ions, solutions of their chloride salts were selected, except for silver and lead (nitrates); for oxy- and chloro-anions, alkali salt solutions were used.

Ascending chromatography was carried out in Perspex or Hellendahl staining jars for a 3-cm run. Solutions of HCl or LiCl (acidified with HCl to 0.15 *N*) were used as the mobile phases. Detection was carried out by spraying with 4-(2-pyridylazo)-resorcinol, dithizone, diphenylcarbazide plus diphenylcarbazone, pyrogallol, potassium iodide, sodium rhodizonate or Chromotropic acid 2R. Details of the experimental procedure and the apparatus required have been reported elsewhere^{6,7}.

RESULTS AND DISCUSSION

Reversed-phase chromatography on silica gel impregnated with the methyl- or phenylpyrazole gave excellent results. The thin layers were of good quality, and the time of run with HCl solutions was only 10–20 min, increasing to 35 min with conc. HCl in the case of the methylpyrazole. When using solutions of LiCl, the development time was 20–60 min. The spots were compact and well formed, except those of Ti(IV), Zr(IV), Mo(VI), Hf(IV), Ag(I) and Pb(II). The tailing that occurred with the first four ions is due to hydrolysis and/or adsorption phenomena⁶. In the case of silver and lead, conversion of the nitrate salts into chloro-complexes probably plays a role.

A large number of the ions investigated did not show appreciable sorption ($R_F > 0.8$) over the whole HCl concentration range used with either of the two pyrazoles. These ions were Be(II), Mg(II), Al(III), Ca(II), Sc(III), V(IV), Cr(III) (often second spot at the origin), Mn(II), Ni(II), Y(III), rare earths and Th(IV). Sb(V) and Au(III) invariably remain at the origin. For all other ions, plots of the R_F vs. HCl normality are presented in Fig. 1. A selected number of plots of R_F vs. LiCl molarity are also included. Several interesting separations are shown in Fig. 2.

The R_F plots show at least a superficial analogy with those previously reported for various amine-Cl⁻ and quaternary ammonium chloride systems^{2,6}. The analogy is most prominent at HCl concentrations above ca. 3 *N*. In this concentration range, the sorption strength of the two pyrazoles appears to be intermediate between those of secondary (Amberlite LA-1) and primary (Primene JM-T) amines, the phenylpyrazole generally being more strongly sorbing than the methylpyrazole. At low aqueous HCl concentrations, a different effect occurs. Generally the R_F values for the methylpyrazole are still closely analogous to those reported for liquid anion exchangers. With the phenylpyrazole, however, the sorption strength decreases considerably and appears to be negligible at HCl concentrations below ca. 1 *N*. The

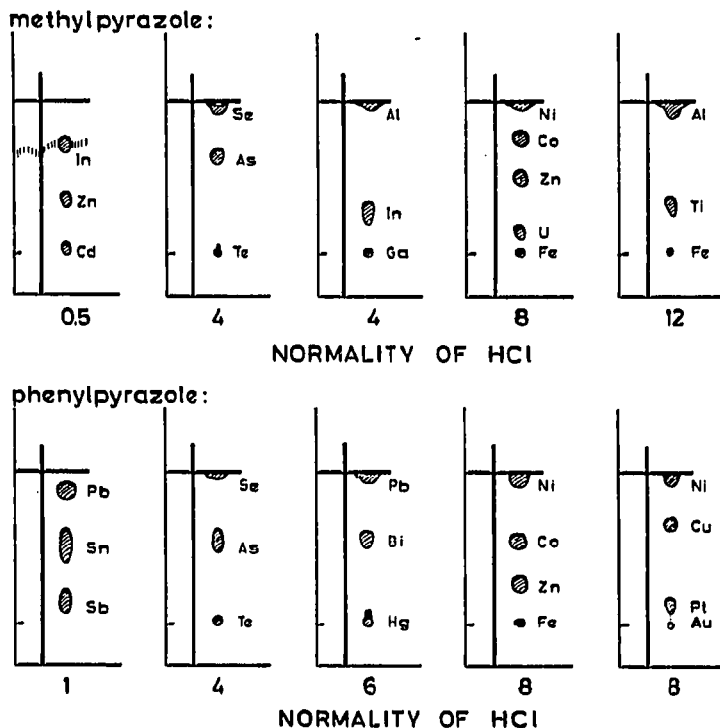


Fig. 2. Examples of separations carried out in the methyl- and phenylpyrazole-HCl systems. The shaded zone in the first diagram indicates the presence of a second front. The mixture of Sn, Sb and Pb was dissolved in 8 N HCl.

seemingly contradictory results obtained with, for example, Zr(IV), Sn(IV), Sb(III) and Hg(II), and especially the unexpected occurrence of maxima in the R_F spectra of the latter two ions, may be explained on the basis of hydrolysis of these ions at very low acid concentrations. This explanation is confirmed by results previously reported for thin-layer chromatography on non-impregnated silica gel⁶.

The diverging behaviour of the methyl- and phenylpyrazoles at low acidity may well be correlated with their extraction efficiency towards HCl. Current investigations in this laboratory indicate that the uptake of HCl by the phenylpyrazole is very low at HCl concentrations up to 5 N, the ratio $(\text{H}^+ : \text{pyrazole})_{\text{toluene}}$ having a value of *ca.* 0.1 at this normality. In contrast, with the methylpyrazole, a value of 1.0 is reached at an HCl concentration of *ca.* 4 N. In other words, the phenylpyrazole is protonated to an insignificant extent only at low acidities, and extraction of anionic metal-chloro complexes does not occur.

Attention may be drawn to the R_F plots observed for Sc(III) and Th(IV). It is well known that the sorption of these ions in amine- Cl^- systems deviates from that in the tri-*n*-octylphosphine oxide (TOPO)- Cl^- system (*cf.* ref. 8). The absence of sorption in the case of amines is attributed to the lack of formation of anionic metal-chloro complexes. With TOPO, however, sorption is due primarily to solvation of neutral metal (oxy)chlorides by TOPO itself instead of to anion exchange by protonated TOPO. Such solvates are easily formed with these ions, which satisfactorily

explains the low R_F values reported for TOPO-impregnated supports. The R_F plots obtained when using pyrazole-impregnated silica gel as the stationary phase strongly suggest that sorption through solvation does not play an important role, thereby pointing to anion exchange as the principal mechanism of extraction.

UV and visible spectra of organic extracts obtained by shaking solutions of the methyl- and phenylpyrazoles in toluene with aqueous solutions of Fe(III), Co(II) and Cu(II) in 8 *N* HCl show that FeCl_4^- (peaks at 318, 366, 450 (shoulder) and 535 nm), CoCl_4^{2-} (698, 666 and 628 nm), CuCl_4^{2-} (310 and 410 nm) and, occasionally, CuCl_3^- (480 nm) are the metal-containing species present in the organic extracts. For the methylpyrazole, the spectra of solutions contacted with FeCl_3 or CoCl_2 dissolved in 8 *M* LiCl and 1–4 *N* HCl have also been recorded. With the former ion, changing the chloride concentration in the aqueous phase does not influence the shape of the absorption spectrum; *i.e.*, FeCl_4^- is the metal-containing species present in the organic extracts in all instances. In the case of Co(II), the spectra in 8 *M* LiCl and 4 *N* HCl are identical with those recorded in 8 *N* HCl. For HCl concentrations below 4 *N*, however, the absorption peaks shift to lower wavelengths. These results demonstrate⁸ that both anionic Co(II)–Cl⁻ complexes (anion-exchange) and CoCl_2 (solvation) are extracted into the organic phase. In summary, anion-exchange is indeed the predominant sorption mechanism. Obviously, however, solvation can play a (minor) role at low HCl concentrations.

Lastly, it is interesting to note that with many metal ions, desorption occurs at high HCl, but not LiCl, concentrations. Most probably, this diverging behaviour may be attributed to the fact that with LiCl, the competition due to the extraction of HCl in excess of the stoichiometric amount occurs to a negligible extent only. The analogous behaviour of pyrazoles and high-molecular-weight amines leads to the suggestion that the excess of HCl is extracted as HCl_2^- (*cf.* refs. 2 and 9). IR analysis will be necessary to confirm this hypothesis.

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