

ANNALES
UNIVERSITATIS MARIAE CURIE-SKŁODOWSKA
LUBLIN—POLONIA

VOL. XXIII, 21

SECTIO AA

1968

Z Katedry Chemii Nieorganicznej i Analitycznej Wydziału Farmaceutycznego AM w Lublinie
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**Partition Chromatography of Metals in Oxo Systems. I. Investigations
of the Parallelism of Equilibrium Partition and Chromatography
Parameters**

Chromatografia podziałowa metali w układach oksoniowych. I. Badanie równo-
ległości równowag podziału i parametrów chromatograficznych

Распределительная хроматография металлов в оксониевых системах.

I. Исследование параллельности равновесий распределения
и хроматографических параметров

Solvent systems employed in paper partition chromatography of metals are often one-phase liquid mixtures of polar solvents and aqueous solutions of acids and salts; the stationary phase is in these cases formed by sorption of more polar components from the developing solvent or tank atmosphere. In recent years, the increasing application of impregnation methods was observed, the reversed phase technique being mostly employed; the paper is usually impregnated with water-immiscible complexing solvents or liquid ion exchangers, such as alkylphosphoric acids or high-molecular-weight amines. Reviews on the application of extraction chromatography were published by Cerrai [1, 2] and Katiykhin [3]. Eliseeva [4] discussed the application of chromatography in the analysis of rare earths. One of the advantages of extraction chromatography is the immiscibility of the two liquid phases, which, on the one hand, permits to determine optimal solvent systems for column liquid-liquid partition chromatography; on the other hand, it permits to estimate the effect of various parameters on partition equilibria and selectivity from easily obtainable paper chromatographic data [1, 2]. The reliability of paper chromatographic data in the latter case depends, however, on the mechanism of the partition processes occurring in the

paper strip. The theoretical relationship between R_F values and extraction coefficients was investigated as early as in the first papers on paper chromatography by Consden, Gordon and Martin [5] (cf. also Bush [6]). A review on this topic was given by Copius-Peereboom [7]; for partition chromatography of metals in liquid ion exchange systems the parallelism of extraction and chromatographic parameters was reported by Cerrai [1, 2], and Waksmundzki and Przeszlakowski [8]. On the other hand, Coch-Frugoni [9], Eliseeva [10], Lauer [11], and Vdovenko [12] investigated the mechanism of chromatographic processes of metals in oxo systems; they found that R_F values calculated from batch extraction data are similar to those obtained in chromatographic experiments, using analogous solvent systems. The analogies show that the decisive mechanism in partition chromatography is distribution between two liquid phases. However, for some systems containing oxo solvents the contribution of additional effects such as adsorption and ion exchange should not be neglected. The decisive role of one of the mechanisms depends on the choice of the solvent. Thus, the mechanism of paper chromatography continues to be an open question, especially for new techniques which are modifications of earlier well known methods.

It follows from the extensive literature on extraction and partition chromatography of metals that the distribution of a metal ion between two liquid phases can be controlled by the choice of the organic solvent or its composition, the concentration and type of ligand in the solution and its pH . From the numerous solvents employed in the chromatography and extraction of metals, water-immiscible aliphatic solvents were chosen for investigation in the present work, the stationary phase being formed by aqueous solutions of ammonium thiocyanate. The effect of concentration of the ligand — thiocyanate ions — on R_F values of some metals was investigated and compared with analogous relationships of static partition coefficients. Moist buffered paper technique was used.

In view of the specific purpose of the investigation the experiments were planned so as to secure maximal analogy of the conditions in chromatographic and bulk extraction experiments, particularly a constant degree of impregnation of the paper; a constant sample size and acidity of the aqueous phase was also maintained. R_M values were calculated from the R_F coefficients from the following equation [13]:

$R_M = \log R_F / (1 - R_F) = \log D + \log r$, where D is the ratio of total concentrations of the metal in the solvent and aqueous phases and r is the ratio of volumes of the two phases ($r = V_{org}/V_w$). The above functional relationship between the partition coefficient D and R_M value shows that the knowledge of the volume ratio r is not indispensable for the

quantitative comparison of chromatographic and static parameters; when it is assumed that r is constant, then R_M and $\log D$ plotted against, e.g., the concentration of the ligand, should give parallel plots (for various experimental techniques and solvent systems, the values of the volume ratio r may be quite divergent [9—12, 14]).

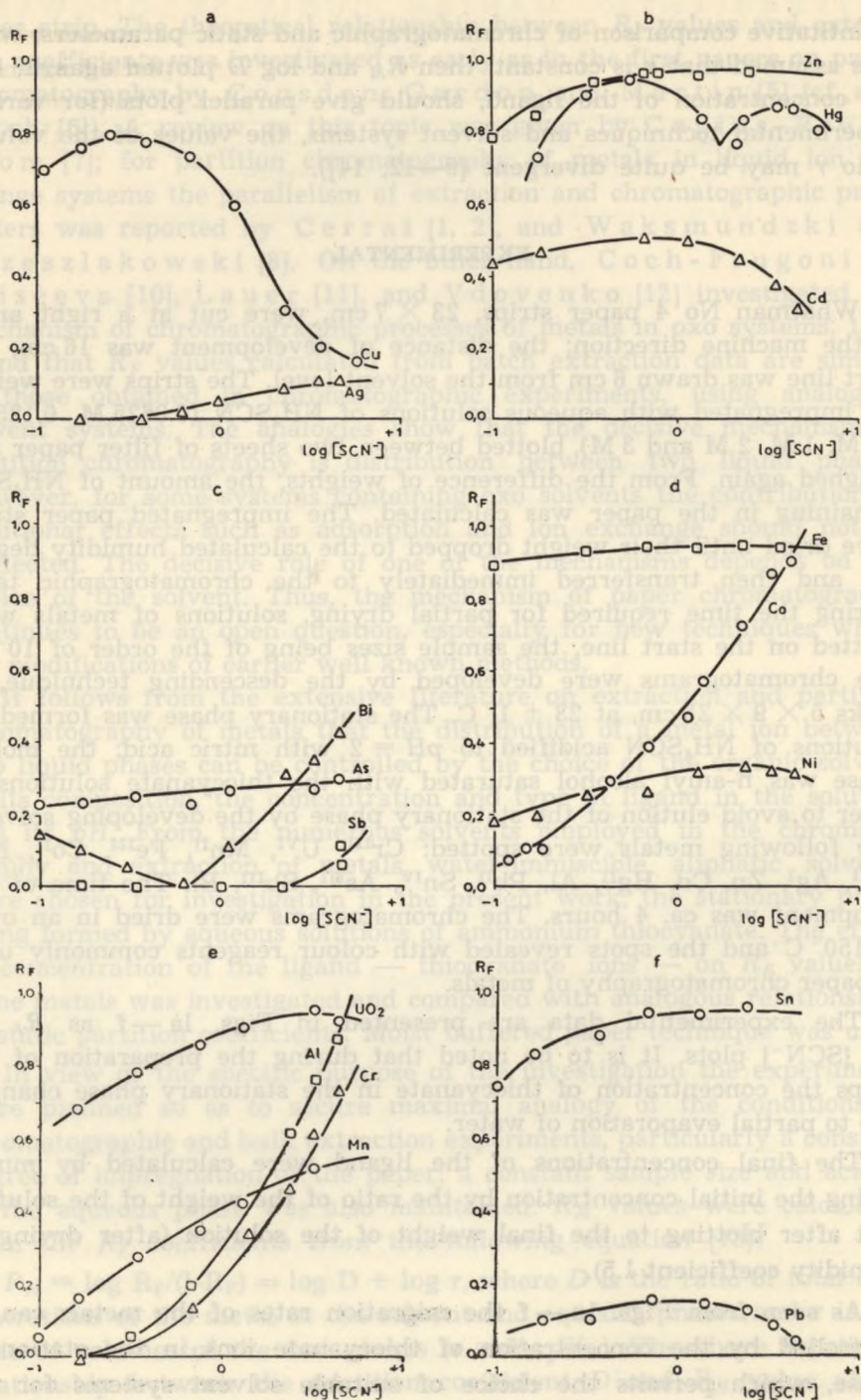
EXPERIMENTAL

Whatman No 4 paper strips, 23×7 cm, were cut at a right angle to the machine direction; the distance of development was 16 cm; the start line was drawn 6 cm from the solvent level. The strips were weighed, impregnated with aqueous solutions of NH_4SCN (0.0625 M, 0.125 M, 0.5 M, 1 M, 2 M and 3 M), blotted between two sheets of filter paper and weighed again. From the difference of weights, the amount of NH_4SCN remaining in the paper was calculated. The impregnated paper strips were dried until their weight dropped to the calculated humidity degree 1.5, and then transferred immediately to the chromatographic tank. During the time required for partial drying, solutions of metals were spotted on the start line, the sample sizes being of the order of 10^{-5} g. The chromatograms were developed by the descending technique, in tanks $5 \times 9 \times 25$ cm, at $23 \pm 1^\circ \text{C}$. The stationary phase was formed by solutions of NH_4SCN acidified to $\text{pH} = 2$ with nitric acid; the mobile phase was *n*-amyl alcohol saturated with the thiocyanate solutions in order to avoid elution of the stationary phase by the developing solvent. The following metals were spotted: Cr^{III} , U^{VI} , Mn^{II} , Fe^{III} , Co^{II} , Ni^{II} , Cu^{II} , Ag^{I} , Zn , Cd , Hg^{II} , Al , Pb^{II} , Sn^{IV} , As^{III} , Sb^{III} , Bi . The time of development was ca. 4 hours. The chromatograms were dried in an oven at 150°C and the spots revealed with colour reagents commonly used in paper chromatography of metals.

The experimental data are presented in Figs. 1a—f as R_f vs. $\log [\text{SCN}^-]$ plots. It is to be noted that during the preparation of the strips the concentration of thiocyanate in the stationary phase changed due to partial evaporation of water.

The final concentrations of the ligand were calculated by multiplying the initial concentration by the ratio of the weight of the solution just after blotting to the final weight of the solution (after drying to humidity coefficient 1.5).

As seen from Figs. 1a—f the migration rates of the metals can be controlled by the concentration of thiocyanate ions in the stationary phase, which permits the choice of suitable solvent systems for the separation of the metals.



Figs. 1a-f. R_F vs. $\log [\text{SCN}^-]$ relationships for the system n-amyl alcohol/aqueous solutions of NH_4SCN ($\text{pH} = 2$).

In order to compare chromatographic and static partition parameters, four metals were selected which gave diverse R_F vs. $\log [\text{SCN}^-]$ relationships, i.e., cobalt, nickel, lead, and zinc. The equilibrium concentrations of the metals were determined by the polarographic method.

Solutions of NH_4SCN were prepared at three concentrations (0.25 M, 1.0 M and 3.0 M), with 0.01% of gelatine, and acidified with nitric acid to $\text{pH} = 2$. The solutions formed at the same time the basic solutions for polarographic determinations; they were shaken for 30 min. with equal volumes of *n*-amyl alcohol and the mixture was left to separate.

The standard solutions of Co^{+2} , Ni^{+2} , Pb^{+2} , and Zn^{+2} ($\sim 10^{-4}$ M) were prepared by diluting concentrated solutions of the salts with solutions of NH_4SCN saturated with *n*-amyl alcohol. Calibration curves were then determined for various concentrations of metals and at various concentrations of thiocyanate ions. Samples of standard solutions were then extracted with equal volumes of *n*-amyl alcohol which had been equilibrated with corresponding thiocyanate solutions. After decantation, the concentration of the metal in the aqueous phase was determined. The concentration in the organic phase was calculated as the difference of concentrations in the aqueous phase before and after extraction.

For Co, Ni and Zn the solutions of NH_4SCN with the addition of gelatine were suitable as the basic solution. Only for Pb the 3 M NH_4SCN was too concentrated and gave a non-linear calibration line. The solubility of oxygen in the solutions was sufficiently low to cause no disturbances in the determinations. It was found that the low amounts of gelatine had no effect on the partition of the metals. The polarographic determinations were carried out using a Type OH-101 Polarograph of Hungarian make.

The static extraction coefficients are plotted in Figs. 2, 3 as. $\log D$ vs. $[\text{SCN}^-]$ plots and compared with R_M vs. $[\text{SCN}^-]$ relationships.

DISCUSSION OF RESULTS

In the system *n*-amyl alcohol-aqueous solutions of NH_4SCN acidified to $\text{pH} = 2$, R_F values of all the metals investigated varied with concentration of thiocyanate ions in the aqueous phase. The only exception was As^{III} , the R_F value of which was ca. 0.20 in the whole composition range studied (cf. Figs. 1a—f). Fe^{III} , Zn and Sn^{IV} had high R_F values even at low concentrations of thiocyanate ions and at concentrations above 0.5 M migrated with the front of the developing solvent. Sb^{III} and Ag^{I} moved from the start line only at concentrations of the ligand above 1 M, their R_F values never exceeding 0.10 (Figs. 1a—c).

Copper showed a R_F vs. $\log [\text{SCN}^-]$ relationship different from that of the remaining metals, its R_F values decreasing with concentration of thiocyanate ions (Fig. 1a). This may be put to reduction of Cu^{II} to Cu^{I} and formation of sparingly soluble complex ions.

Mercury^{II} also gives a non-typical R_F vs. $\log [\text{SCN}^-]$ relationship (Fig. 1b), with three extremums: two maxima corresponding to ca. 0.6 M and 4 M solutions of thiocyanate and a minimum at 1.5 M. This behaviour of mercury is probably caused by shifting formation equilibria of various thiocyanate complexes of mercury; similar irregularities were also ob-

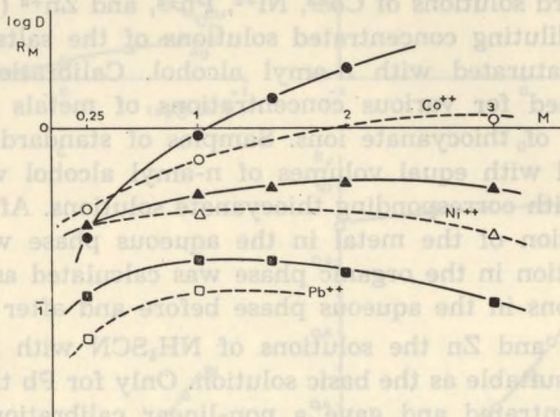


Fig. 2. Comparison of paper chromatographic data (continuous lines) with static $\log D$ vs. $[\text{SCN}^-]$ relationship (dashed lines) obtained from polarographic determination for lead, nickel and cobalt for the system *n*-amyl alcohol/aqueous solutions of NH_4SCN

tained when iso-amyl, hexyl alcohol, and cyclohexanol were used as the mobile phase; the occurrence of minima was also reported by Plaksin et al. [15] for batch extraction experiments in analogous systems. Bismuth^{III} also gives a similar relationship (Fig. 1c).

The R_F vs. $\log [\text{SCN}^-]$ relationships show certain analogies to static $\log D$ vs. $\log [\text{SCN}^-]$ relationship obtained for similar systems [16, 17, 18].

In Fig. 2 R_M vs. $[\text{SCN}^-]$ relationships of Co, Pb, Ni are compared with $\log D$ vs. $[\text{SCN}^-]$ relationships obtained from static (batch) partition experiments. A certain parallelism of chromatographic and static partition parameters is observed, although pairs of curves are not strictly parallel. In Fig. 3 static $\log D$ vs. $[\text{SCN}^-]$ relationships of cobalt, reported by Brubaker and Johnson [19], for the system: *n*-hexyl alcohol/ $\text{NaSCN} + \text{NaClO}_4$ (constant ionic strength, at two values of pH), are compared with our chromatographic data for a similar system: *n*-hexyl alcohol/aqueous solution of NH_4SCN acidified with HNO_3 to

pH 3 [20]. Although the batch and chromatographic systems are not identical, good parallelism is observed.

It seems, therefore, that chromatographic data for the technique employed, apart from practical significance, may also provide information concerning static partition parameters, particularly on the effect of ligand concentration, ligand type, structure of oxo solvent, effect of diluting solvent, mechanism of partition etc. Occasional discrepancies may be largely due to the following causes.

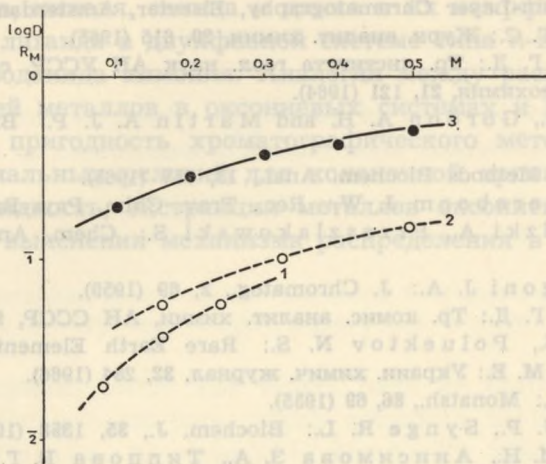


Fig. 3. Comparison of static (1, 2) and chromatographic (3) partition parameters. Mobile phase: n-hexyl alcohol. Polar phase: 1 — $[H^+] = 0.500$, solutions of $NaSCN + NaClO_4$ of constant ionic strength 1.5; 2 — as before, $[H^+] = 0.750$; 3 — $[H^+] = 0.01$, aqueous phase — solutions of NH_4SCN , varying ionic strength. Log D: hollow points, dashed lines [19]; R_M : full points, continuous lines [20].

1. Nonlinearity of partition isotherm of the metal.
2. Contribution of adsorption effects of cellulose and its effect on the properties of the fixed phase.
3. Kinetics of the chromatographic process.
4. Variation of the volume ratio of the two phases (r).

It seems that the last factor might cause the lack of strict parallelism of $\log D$ and R_M values in Figs. 2, 3; although the impregnation degree was constant in the chromatographic experiments, the solubility of water in the alcohol phase increases with concentration of NH_4SCN , especially at concentrations of NH_4SCN above 2 M (cf. *Dombróvskaya and Bondarenko* [21]); the increase of the volume of the organic phase entails the increase of the volume ratio, and that could be the reason why the pairs of cor-

responding R_M vs. $[\text{SCN}^-]$ and $\log D$ vs. $[\text{SCN}^-]$ lines tend to diverge to the right (since for a given metal $R_M - \log D = \log r$). In further systematic experiments attempts were made to eliminate this effect.

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STRESZCZENIE

Badano zależność zmian $\log D$ wyznaczonego z danych statycznych i wartości współczynników R_M od stężenia ligandu dla kobaltu, niklu, ołowiu i cynku w dwufazowym układzie typu alkohol n-amyłowy — wodny roztwór rodanku amonowego. Analogia pomiędzy chromatografią podziałową metali w układach oksoniowych i ich ekstrakcją wskazuje

na przydatność metody chromatograficznej do badania optymalnych warunków dla podziałowej chromatografii kolumnowej ciecz — ciecz, dla ekstrakcji metali z rozpuszczalników oksoniowych, jak również do wyjaśnienia mechanizmu podziałowego w tych układach.

РЕЗЮМЕ

Исследовалась зависимость логарифма коэффициента распределения кобальта, никеля, свинца и цинка и их коэффициентов R_M от концентрации лиганда в двухфазной системе типа *n*-пентанол — водный раствор роданида аммония. Аналогия между распределительной хроматографией металлов в оксониевых системах и их экстракцией указывает на пригодность хроматографического метода для исследований оптимальных условий для колоночной хроматографии типа жидкость — жидкость, экстракции металлов оксониевыми растворителями и для выяснения механизма распределения в этих системах.

Распределительная хроматография металлов в оксониевых системах.
И. Смирнов в качестве экстрактивов роданидных комплексов металлов

Alcohols, ketones, esters and ethers form an individual group of extractants called oxo solvents, which according to the classification proposed by Fomin (1) belong to chemically neutral extractants. Their extraction properties are due to the formation of extractable coordination compounds with simple complexes of metals; e.g. with thiocyanate complexes. Solvent systems composed of oxo solvents and aqueous solutions of thiocyanates are often employed for chromatographic and extraction methods of separation of metals [2—13].

In recent years the search for selective partition systems is mainly focused on multicomponent solvents, composed of mixtures of oxo solvents [14—17] or mixed extractants in which alcohols, ketones or esters are diluents for active solvents which extract metal ions or their simple complexes by the liquid ion exchange mechanism [18—20] or as neutral high-molecular weight extractants (e.g. tributylphosphate) [17, 21]. In all these cases it is useful to understand the effect of the diluting solvent on the partition behaviour of metals during extraction with mixed organic solvents.

In the previous part [22] it was demonstrated that in the "mixt paper" technique, in solvent systems of the type oxo solvent/aqueous electrolyte solution, the decisive process in chromatography is liquid

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STRESZCZENIE

Badano zależność zmian $\log D$ wyznaczonego z danych statystycznych i wartości współczynników R_d od stopnia ligandu dla kobaltu, niklu, miedzi i cynku w układach...

Pracę wykonano w Zakładzie Chemii Analitycznej, Uniwersytecie Warszawskim, w Warszawie, w 1964 r.