The Determination of the Distribution Coefficient the Selectivity Coefficient and the ion Exchange Energy by the Automatic Thermodetective Type Liquid Chromatography

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1 Introduction

It is common sence that ion exchange chromatography is one of the most valuable separation method for metal ions. Several theoretical works for ion exchange chromatography such as the determination of distribution coefficients and kinetics, and applied works such as industrial separation of rare earth elements and preparation of salts from marine water can be found in many recomended books. [1][2]

It is very meaningful to determine distribution coefficients in some media in that it gives to us the information whether to separate or not, but it is very troublesome works to determine them in both cases of the batch and the column method.

We could devise the easy determination method of distribution coefficient, using the automatic thermodetective type liquid chromatography.

In this report, distribution coefficients of various metals for strong acid type cation exchange resin in 2 M hydrochloric acid media is reported. Futhermore, this appratus is used as micro calorimeter so that the chealation energy of copper (11) with EDTA, and ion exchange energy of copper (11) with potassium ion in resin are determined. Those results are reported.

2 Experiment

2, 1 appratus

The appratus which is used for determination of distribution coefficients, selectivity coefficients and chemical energy was JRC-1 type automatic thermodetective type liquid chromatography made by Nippon denshi., Co, Ltd.

The block diagram in the case of the application for normal ion exchange chromatography is shown in fig 1. As shown in fig 1 effluent solution is flown into the detection column through the reference column and the separation column by the constant current liquid pump.

Sample solution for analysis is introduced to the separation column by exchanging balb between the reference column and the separation column, separated in the separation column and introduced into the detection column. In the detection column, the thermal exchange due to ion exchange to the reference column is recorded. The flow rate of effluent in this case is 0.8 ml/minutes.

The block diagram for determination of chemical energy is shown in fig 2, As mentioned in fig 2, the effluent is flown into the detection column directly through the reference column.

In case it is used as chromatography, each column is filled full with resin, but for energy determination, in both column of the reference and the detective, 0.2 ml of resin sandwitched
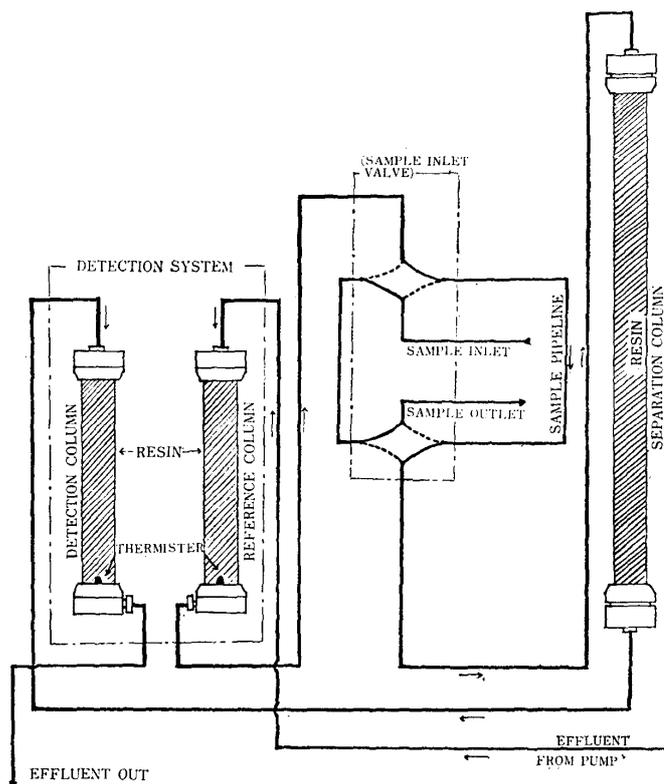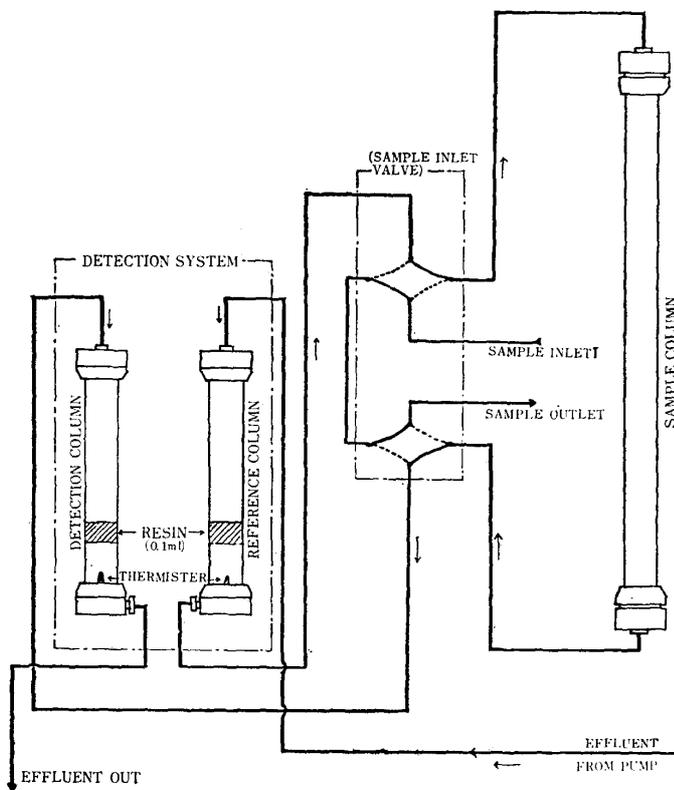
Fig. 1 The block diagram for iou exchange Chromato graphy

Fig. 2 The block diagram for determination of chemical eneryy

in glass beads is packed. Futhermore, in the detection column plutinum foil coil of 0.1 mm in diameter and 10cm in length, havingl. 11Ω electric resistance is arrainged so that the application of proper amounts of energy, nearly corresponding to ion exchange or chealation energy, is possible in the detection column.

2, 2   reagents and ion exchange resin

Guaranteed grade of metal chloride was dissolved in dilute hydrochloric acid for metal chloride stock solution and its concentration was determined by chealatemetric titration. All the other reagents such as hydrochloric acid as effluent and EDTA as chealatemetric titration reagent were guaranteed reagents without furification.

The ion exchange resin which was used is Dowex 50WX4 (50～100 mesh) The resin, preliminalily, was treated with proper concentration, for instance, 2M, hydrochloric acid, washed by deionized water and packed into the each column, but in the determination of chemical energy, potassium resin was packed in columns.

2, 3   determination of distribution coefficients and selectivity coefficients

When the volume distribution coefficent for ion exchange resin is determined by the column method, it is well known that the relation equation is as follow.

$$Kd = \frac{Vm}{A \times L} - \alpha \qquad (1)$$

In the equation, Kd is the volume distribution coefficient, Vm is the volume of effluent which moves the maximum concentration of the band of the sample for analysis, L is column length, A is the cross section area, and α is the specific void fraction for the column. In the automatic thermodetective type liquid chromatography, after sample was introduced into the separation column, some time the thermogram by effluent (generally so-called and discussed in detail in my other report) appears in the recorder.

The volume of effluent which is eluted untill the appearence of the thermogram by effluent is the void volume in the column employed. So the equation (1) is rewritten as follow.

$$Kd = \frac{v(t - t_0)}{A \times L} \qquad (2)$$

In the (2) equation, v is the flow rate of effluent, t is the retention time in minutes and t_0 is minutes of appearence of the thermogram by effluent.

The following equation is known as the relation between the distribution coefficient and the selectivity coefficient.

$$K = Kd \left\{ \frac{(M)}{(RM)} \right\} \qquad (3)$$

In the equation (3), (RM) is the specific ion exchange capacity for employed resin and (M) is the concentration of effluent.

2, 4   the determination of ion exchange energy and chealation energy

When chemical energy such as ion exchange energy of copper (II) with potassium ion in resin is determined, potassium type ion exchange resin is packed in the detection column and the reference column.

After non conditioning noise in the recorder diappeared by columns being washed, a proper amount of Joule energy is generated in the detection column by charging plutinum foil coil with electric cell and thermal exchange in the detection column to the reference is recorded.

In the next experiment, a proper concentration of copper (11) solution is introduced only into the detection column while water is flown into the reference by balb exchange. Then the thermal exchange due to ion exchange in the detection column is recorded to the reference. The integlated value of the ther-mogram in the recorder by ion exchange is compared with the value by Joule energy and ion exchangeenergy is determined. Futhermore, by balb exchange a proper concentration of potassium chloride solution is introduced into the detection column and the energy for the reverse ion exchange reaction is determined.

In the determination of the other chemical energy, same experiment is persued.

3 results and discussion

3, 1 distribution coefficients of various metals in 2M hydrochloric acid

To determine distribution coefficients, various metal ion were eluted through the column, 50 cm in length and 0.8 cm in diameter by 2M hydrochloric acid solution. A part of thermo-rgams, obtained in the recorder as results, is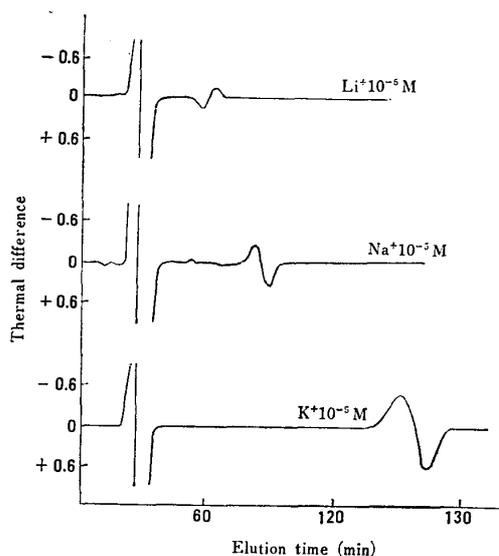 shown in fig 3. As apparent in fig 3, first the thermogram depending on physical adsorption of the effluent, 2 M hydrochloric acid, appears in 18 minutes after introducing each sample metal ion and meanwhile the thermogram depending on ion exchange of metal ion with hydronium ion appears.

The possition of the latter thermogram is particular to each ion and the cross point of the base line shows the retention time and the retention volume of each ion for column. For instance the retention time for lithium corresponds to 61 minutes, for sodium is 81 minutes and for potassium is 159 minutes. Also it is clarified that the retention time for alkali earth such as calcium strontium and barium are extrodinarily great. The quantitative analysis can be carried out by the calibration curve between the concentration of sample and the amplitude of the thermogram by ion exchange. These value, obtained by the experiment, are shown in table 1.

Fig. 3 Thermograms for alkali metols by 2MH ydrochloric acid.

The magnitude of amplitude per 1 m M shows the sensitivity of the quantitative analysis for each metal sample by this method, though these values change by the column length and the concentration of the effluent.

The retention time for each metal, the time 18 minutes which is necessary for the appearence of the thermogram by the effluent after the addition of the sample, which is common to eahc metal, the flow rate of the effluent 0.8 ml/minutes and the column dimension

Table 1 Chromatographic constants of various metal ions by
2M hydrochloric acid effluent

ion	retention time (min)	magnitude of amplitude (cm)
Li	61	1.6
Na	84	2.4
K	159	2.84
Mg	144	0.4
Ca	225	2.0
Sr	305	3.2
Ba	744	4.9
Fe	100	7.9
Ni	112	4.9
Co	120	3.4
Al	196	
Cu	83	

25 ml are introduced into the equation (2) so that distribution coefficients are determined.

The selectivity coefficient can be determined by the equation (3) using the distribution coefficients, the concentration of the effluent and the specific ion exchange capacity of resin 2.8meq/ml. The results are tablated in table 2. We can estimate easily by the possibility of separation from this values.

Table 2 Distribution coefficients and selectivity coefficients

ion	distribution coefficient	selectivity coefficient
Li	1.12	0.78
Na	1.80	1.25
K	4.40	2.83
Mg	3.58	2.51
Ca	6.10	4.21
Sr	8.39	5.87
Ba	21.4	14.9
Fe	2.27	1.57
Ni	2.63	1.64
Co	2.87	2.01
Al	5.13	3.59
Cu	1.79	1.25

3, 2 the determination of ion exchange energy and chealation energy

3, 2, 1 the thermogram by Joule energy; To determine as energy thermal exchange in the detection column due to generation of heats, the relation between generated heats and integlated values of thermograms in the recorder by Joule energy is discussed. That is to say, various quantities of stepwise Joule energy is generated in the detection column by electrifying the plutinum foil coil and thermograms due to it is recorded. the relation between integlated values and corresponding Joule energy is shown in fig 4. As mentioned in fig 4, a strait line plots
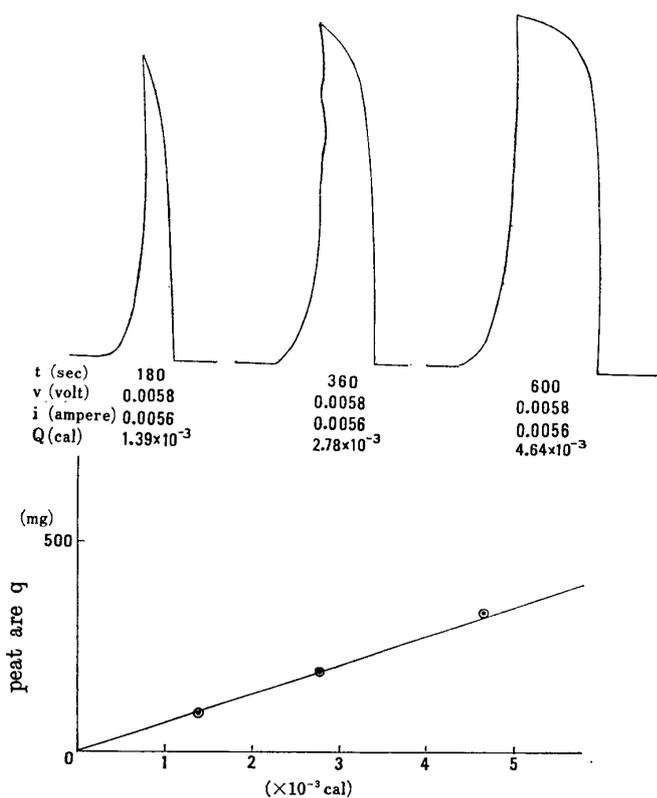
t (sec)	180	360	600
v (volt)	0.0058	0.0058	0.0058
i (ampere)	0.0056	0.0056	0.0056
Q (cal)	1.39×10^{-3}	2.78×10^{-3}	4.64×10^{-3}

(mg)
500

peat are q

0   1   2   3   4   5
$(\times 10^{-3} \text{cal})$

Fig. 4 The relation between Joule energy andinteglated values of ther mograms

⊖
→
⊕

Sample
CuCl₂ 1×10⁻² M (f=0.967) 1ml
Resin
K—form 0.2ml
Set sensitivity
$30° \pm \frac{3}{1000}$°C

⊖
→
⊕

Sample
CuCl₂ 1×10⁻³ M (f=0.967) 1ml
Resin
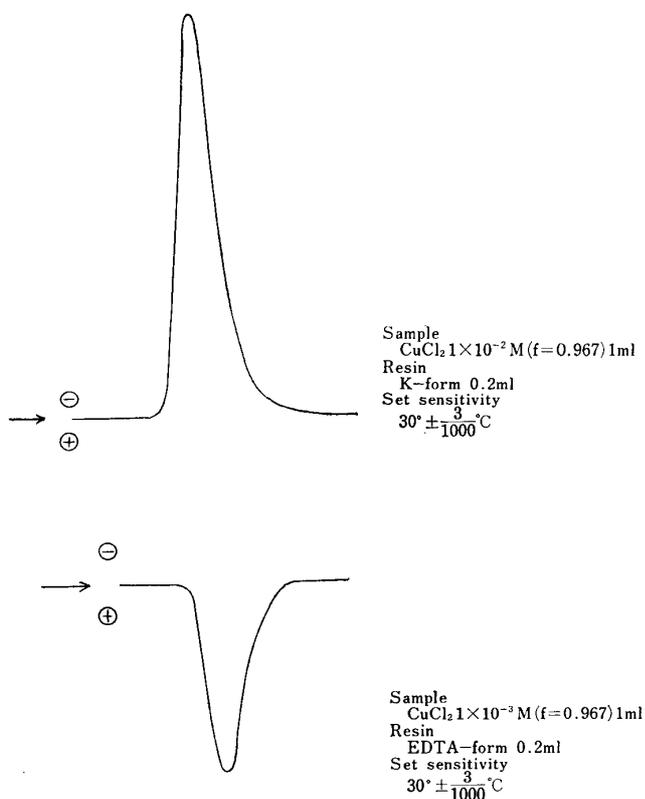EDTA—form 0.2ml
Set sensitivity
$30° \pm \frac{3}{1000}$°C

Fig. 5 thermogram by ior exchange

are formed, for it is shows that integlated value is proportional to Joule energy generated in the detection column. Various chemical energys can be calculated by this calibration line.

3, 2, 2 ion exchange energy of copper (II)

As above mentioned, 0.2 ml of potassium type resin is packed in the detection column and the reference column. While water being flown into the reference column, 1 ml of solution containing 0.976×10^{-2}M copper (11) is flown into the detection column. In the column, ion exchange reaction of copper (11) with potassium ion in the resin occurs so that the thermogram appears in the recorder as result. The result is shown in fig. 5.

The energy corresponding to the integlated value of the thermogram in fig. 5 is determined by using the calibration curves in fig. 4 and the energy for the following chemical equation is calculated as −355 cal

$$2R K + Cu^{2+} \rightarrow R_2 Cu + 2 K^+$$
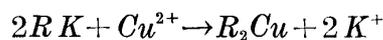
3, 2 3 The chealation energy of copper (11) for EDTA

A plenty volume of 10^{-1}M EDTA solution is flown into the detection and the reference column s, which are packed with 0.2 ml of strong base type anion exchange resin Dowex 1×4, so that the chloride type resin is converted to the EDTA type resin. In the next experiment, a large quantity of water is flown into the both columns untill the disappearence of noise in the recorder and 1 ml of solution containing 0.967×10^{-3} M copper (11) is flown into only the detection column while flowing water into the reference column by balb exchange.

The thermogram due to the generation of energy is recorded. The result is shown in fig. 5.

The energy corresponding to the integlated value is determined by the calibration line in fig 4 and the energy for the following chemical equation is calculated as 1.45×10^3 cal

$$R - EDTA^{=} + Cu^{2+} \rightarrow R - EDTACu$$
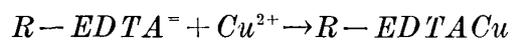
In this reaction, it seem that the resin acts as the suporter of $EDTA$ so that this enegy is nearly equal to the chealation energy of copper (11) with $EDTA$.

Literature

1) J. Inczedy Analytical Application of lon exchangers. Pergamon Prers (1966)

2) W. Ricman Ⅲ. and H. F. Walton Ion Exchangers in Analytical Chemisty Pergamor Prers (1970).