Selective Ion Exchange Resin

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With the progress of atomic and other rising industries, new materials are of ever increasing necessity. Some of these materials are the special metals which have never widely been used in industry. These metals often occur in ores, rocks, water in very small amounts. New methods of separating these metals should be developed in future.

In 1935, Adams and Holmes[1] observed that certain synthetic resins were capable of exchanging ions. The versatility of these resins was rapidly recognized by many academic and indudustrial chemists, with the result that a large number of new and unique uses were found for ion exchange resins and many attempts were made to modify and improve these resins. The utilization of ion exchange resins for separation, recoveries, deionization, catalysis, as well as water softening on an industrial scale has become a reality.

It must be a good idea to use ion exchange resins for the purpose of separating of metals. It is still very hard to get the resins suitable for the separation of metals in the advanced fields of industry, but the study of the resins for the separation of ordinary heavy metals will be a milestone for above purpose.

This study was undertaken in order to find the resins suitable for this purpose and the conditions in which the separation of small amounts of metals is well done.

An exact empirical expression[2] describing the exchange reaction is

$$\frac{(M_2)_R}{(M_1)_R} = K \left[\frac{(M_2)_S}{(M_1)_S}\right]^n \qquad n<1 \ (K>1)$$

Where the subscripts refer to the resin and external phases when two cations M_2 and M_1 are present.

If a large excess of M_2 is present, the ratio $(M_2)/(M_1)$ must become very large, so it is very difficult to recover M_1 from the solution containing small quantity of M_1 and large quantity of M_2 by these cation exchange resins.

Anion exchange resins can absorb metals in the form of complex with aid of other anion.

The recent development of ion exchange resins that exhibit unusual selectivity towards certain ions has received considerable attention. As selective ion exchange resins, chelate resins occupy an important position. So many kinds of chelate resins were chiefly studied in this paper. The chelating reactions in synthetic high polymers have a close relation to the

chemical reactions in natural proteins and other organic high polymers.
    As selective adsorption resin, the following resins were studied here,
        A.   Amphoteric ion exchange resins
        B.   Chelate resins
        C.   Phenyl arsonic acid resins
    The course of the study is divided into the following two parts.
        Part   I.   Synthesis of chelate resins and adsorption of metals by these
   resins
        Part   II.   Physical chemistry of chelating reactions in resins

Part   I

A.   Amphoteric Resins[3]
 I.   Determination of ion exchange capacity of amphoteric resins. [4]
    It is very difficult to determine the exchange capacities of amphoteric
resins for cation and anion at the same time. If amphoteric resin is made
hydrogen form with HCl, HCl is adsorbed at basic groups. Therefore, if
we determine the cation exchange capacity of amphoteric resin as usual, not
only adsorption of NaOH by acidic groups but also neutralization of NaOH
with HCl adsorbed by basic groups will be occurred. As for anion exchange
capacity, we can not get the true value of it.

$$\underset{\overset{|}{R}}{\overset{NH_2 \; HCl}{|}} \!\!\!\!\!\!\! \begin{array}{c} \\ \\ COOH \end{array} + 2\,NaOH \rightleftharpoons \underset{\overset{|}{R}}{\overset{NH_2}{|}} \!\!\!\!\!\!\! \begin{array}{c} \\ \\ COONa \end{array} + NaCl, \quad \underset{\overset{|}{R}}{\overset{NH_2}{|}} \!\!\!\!\!\!\! \begin{array}{c} \\ \\ COONH_4 \end{array} + 2\,HCl \rightleftharpoons \underset{\overset{|}{R}}{\overset{NH_2 HCl}{|}} \!\!\!\!\!\!\! \begin{array}{c} \\ \\ COOH \end{array} + NH_4\,Cl$$
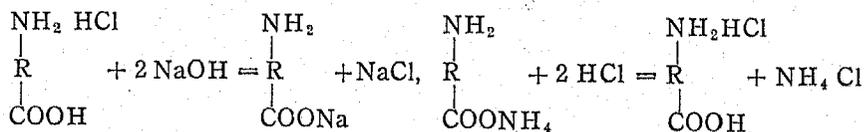
According to Mattson and his students, [5] the pH titration curve aids in the
determination of acidity or basicity of the exchange group, the total number
of exchange groups and the number of types of exchange groups present.
This method can be applied to anion or cation or amphoteric substances. But
we must use comparatively a large quantity of resin and also spend a
longer time. So it is not good for the simple determination of exchange
capacity. The true cation or anion exchange capacity may be determined
from the quantity of Cl^- or NH^+_4 left in the solution for which we calculated
the ordinary exchange capacity.
1) Cation Exchange Capacity
    In order to regenerate the acidic groups in resin, H_2SO_4 or HCl is chiefly
used. HCl is an excellent regenerant and is more easily be determined than
H_2SO_4 in chemical analysis.
  (1) Procedure
        Steep 1 g. of resin in 30 ml. of 10% HCl[6] for one hour, wash it
    with water until Cl^- is not detected, then add 20 ml. of 0.5 N NaOH into
    it, stir for one hour and wash it several times with total 200 ml. of water.
    (last steeping is done over night). Titrate the NaOH left in the washed
    solution with HCl and determine the quantity of Cl in this titrated solution.

The deduction of the quantity of Cl⁻ in the HCl which was used to neutralize the NaOH from the quantity of Cl⁻ in the titrated solution gives the quantity of HCl adsorbed at basic groups. The true cation exchange capacity may be calculated by this method.

(2) Determination of Chlorine

Gravimetric and volumetric methods are used for the determination of chlorine. Volumetric method is considered to be more convenient than gravimetric one for this purpose. Add the excess of $AgNO_3$ over Cl⁻ to this solution and titrated the excess Ag^+ left with KCNS using Fe-alum. NaOH or HCl is standardized with oxalic acid or sodium carbonate, while KCNS is with $AgNO_3$. The relationships between NaOH or HCl and KCNS should previously be established.

(3) Results

The results are shown in table I

Table 1

	Hexamethylenetetramine Furfural resin				Phenolsulphonic acid HCOH resin	
	A1	A2	B1	B2	C1	C2
NaOH m. M/g. resin	4.03	4.49	4.73	4.70	5.11	5.15
Cl ″ ″	0.95	1.05	1.09	1.09	0.005	0.04
Cation Exchange Capacity m. M/g. resin	3.08	3.44	3.84	3.64	5.105	5.11

II) Anion Exchange Capacity

As a regenerant of anion exchange groups, NaOH or NH_4OH is used. In order to regenerate strong basic groups, we must use strong alkali but for weak one we may use weak alkali. The low equivalent weight and the low cost of NH_3 have made this base preferable regenerant.

This is the same to amphoteric resin and NH_4^+ is more easily determined than Na^+ in chemical analysis.

(1) Procedure

1 g. of amphoteric reisn is changed into hydrogen form with HCl, then steep in NH_4OH solution to regenerate anion exchange groups and wash with distillated water until NH_4^+ is not detectable. Add 20 ml of 0.5 N HCl, stir for one hour, wash with water as in the case of the determination of cation exchange capacity.

Titrate the HCl left in the solution with 0.1 N of NaOH. NH_4^+ in the solution is measured by semimicro Kjeldahl method. From the quantity of HCl consumed, deduce the quantity of NH_4^+ in the titrated solution and this will give the quantity Na^+ adsorbed at acidic groups. The concentration of NH_4^+ in the washed solution is so small that the titrated solution is acidified with concentrated H_2SO_4 and is condensed.

(2) Results

The results are shown in Table 2

Table 2

m. M/g. reisn	m-phenylenediamine furfural resin				Hexamethylene-tetramine furfural resin						Anilin HCOH resin			p-phenol sulpho-nic HCOH		Furfural resin	
	A1	A2	B1	B2	A1	A2	B1	B2	C1	C2	1	2	3	1	2	1	2
HCl consumed	0.82	0.85	1.01	1.00	2.50	2.67	2.74	2.73	3.10	3.25	1.04	1.10	1.06	1.86	1.83	2.60	2.66
NH_4^+	0.31	0.35	0.42	0.42	0.07	0.08	0.09	0.10	0.01	0.01	0.00	0.05	0.03	1.85	1.83	2.67	2.69
Anion Exchange Capacity	0.51	0.50	0.59	0.58	2.43	2.59	2.65	2.63	3.00	3.15	1.04	1.05	1.03	0.01	0.00	0.00	0.00

p-phenolsulphonic acid HCOH resin or furfural resin does not have anion exchange groups and their acidic groups were changed into SO_3NH_4 or $COONH_4$ with NH_4OH, therefore all the NH_4^+ ions in acidic groups were removed to the solution with HCl in the determination of anion exchange capacity. Their anion exchnge capacities were nearly zero as we expected. The quantity of NH_4^+ in the titrated solution in the case of anilin resin was small and this is easily understood by the fact that this resin does not have acidic group. As to amphoteric resin, the quantity of NH_4^+ in the titrated solution was smaller than that of expected from the content of COOH group. This is probably because of having both acidic and basic groups in them. m-phenylenediamine furfural resin lies between amphoteric and furfural resins about NH_4^+ content. Partial sulphonation might have been occurred in m-phenylenediamine.

II. Regeneration of Amphoteric Resins. [7]

The difficulties in regenerating amphoteric resin is a vital obstacle. It is well known that weak acid will hardly react with weak base, so will it be with amphoteric resin having weak acidic and basic groups.

Judging from the result in table 2, only a small portion of COOH groups in hexamethylenetetramine-furfural resin were in COONH$_4$ form, when it was treated with NH_4OH to regenerate NH_2 groups in them. The combination of treatment with HCl and that with NH_4OH makes it possible to regenerate both acidic and basic groups.

1) Procedure

Put hexamethylenetetramine furfural resin into 10 % HCl solution, wash it with water, then put into 10 % NH_4OH and finally wash thoroughly with distillated water. In order to know whether both acidic and basic groups in this resin are regenerated or not, exchange capacities were determined.

2) Results

The results are shown in Table 3.

Table 3

Cation Exchange Capacity	Sample			
	No. 1	No. 2	No. 3	No. 4
A	2.42	2.26	2.50	2.28
B	2.42	2.20	2.45	2.39

Sample used were prepared in the different reaction vessels (No. 1—4). Column A is correspond to cation exchange capacity of the resin treated with only HCl and washed water, Column B to that of the resin treated with HCl and NH$_4$OH, and washed with water. A good agreement between A and B was seen in the table.

III.   Tyrosin Resin[8]

From the structural point of view, Tyrosin will be able to form the resin which has chelate forming property and has a net structure in which ions can easily move. So it is considered to be a good raw materials of ampho-teric resin.

1) Synthesis of Tyrosin Resin

Synthetic tests were made under the following conditions.

(1) Tyrosin + HCOH + acid or alkali catalysers.

(2) Tyrosin + Phenol + HCOH + acid or alkali catalysers.

(3) Tyrosin + Resorcine + HCOH + acid or alkali catalysers.

A good resin was obtained from tyrosin, phenol, HCOH and NaOH catalyser. This resin was not soluble in water, acid and alkali and was mechanically stable enough to be of practical value. Preparation of Tyrosin-Phenol Resin : Dissolve 8 g. of tyrosin in NaOH solution, add 8 g. of phenol to this solution. The mixture was reacted with 26.5g of HCOH (35%) at 90°C. The resin was crushed and dried at 110°C. and finally washed.

2) Conditioning of Resin[9]

The resin was ground and screened to 30 to 40 mesh size, and was treated continuously with 0.1 N NaOH. After rinsing with water, 0.1 N HCl was used for washing the resin as in the case of NaOH Finally, the resin was washed with 0.1 N KCl. The washing with water was continued until only a trace of Cl ion appeared. The resin was then air dried and its moisture content determined over P$_2$O$_5$. This resin has an exchange capacity of 2.18 m.eq., cation /g. resin and that of 1.75 m. eq. anion /g. resin. The pH titration curves of these resins show that the quantity of amino group decreased and the new group appeared.

Anthranilic acid-phenol (1:1 mol.) resin was used for the comparison of Tyrosin resin on adsorbability of metals.

3) Adsorption of metals by resin[10]

All experiments were carried out by shaking of known amounts of various solution with weighed samples (0.5g) of resin in a flask at room temperature for 48 hrs., followed by analysis of an aliquot of the equilibrating solution. The amount adsorbed was reported as millimoles of metal adsorbed per gr.

of dried resin. This quantity was calculated from differences in the initial
and final concentrations of the metal ion under investigation. Buffer solutions
were used to set the pH of the equilibrating solutions. Co, Hg, Cu and Cd
were used in these experiments. The adsorption of Co increased with increase
of pH value in both resins. Hg was adsorbed by anthranilic acid resin as
much as 1.0 m. eq/g., while tyrosin resin slightly adsorbed it, in Fig. 1.
The distance between amino group and carboxylic group of anthranilic acid is
larger than that of tyrosine. The distance between these groups in tyrosine
must be too small to accomodate such a large ion. Ionic radius of Hg is
known to be 1.12 Å and that of Co is 0.8 Å. The effect of dilution on
adsorbability by anthranilic acid resin was shown in Fig. 2. Since the metals
were absorbed to different extent at different pH levels, separations can be
readily effected in favorable cases. Cu was absorbed by Tyrosin resin over
a wider pH range beyond the max. point at pH 2. Adsorption of Co by
tyrosin resin became more and more as the pH increases beyond at PH 2.
Hg was not adsorbed over wide pHᵢ range by Tyrosin resin. Adsorption of
Co by anthranilic acid resin increases as the pH increases. Hg showing
adsoption over wider pH range had a maximum at pH 4. The absorptive
capacity of the anthranilic acid resin increased with the concentration of
the metal ions having the maximum at the same pH value in each case.
From the pH titration Curve, cation and anion exchange capacity, nitrogen
content, and synthetic conditions, unit structure of tyrosin may be assumed
as follows

Fig. 1 Adsorption of Metal Ions by Tyrosin Phenol Resin
○Co   Total Co 2.11m. Mol
△Cu   Total Cu 2.0 m. Mol
●Hg   Total Hg 2.21 m. Mol
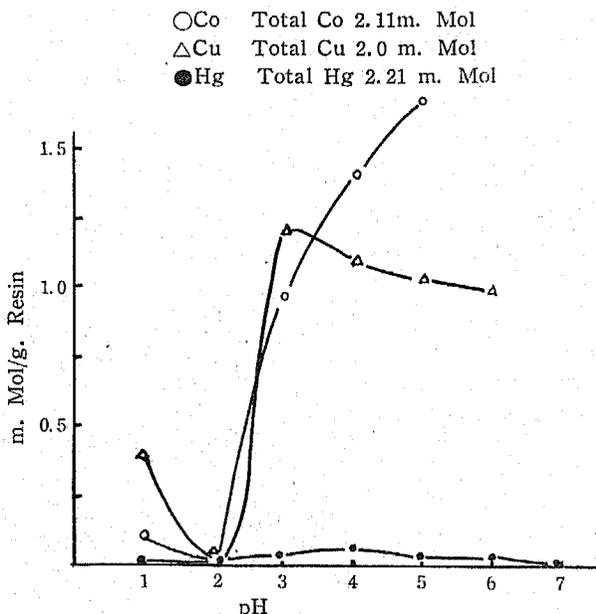
Fig. 2   Adsorption of Metal Ions by Anthranilic Acid-Phenol Resin.

     ●   Hg   0.06 M Solution (Total 2.22 m. Mol)
     ●   Hg   0.04 M Solution (Total 1.11 m. Mol)
     ○   Co   0.06 M Solution (Total 1.692 m. Mol)
     ○   Co   0.035 M Solution (Total 0.82 m. Mol)
     ×   Cd   0.025 M Solution (Total 1.0 m. Mol)
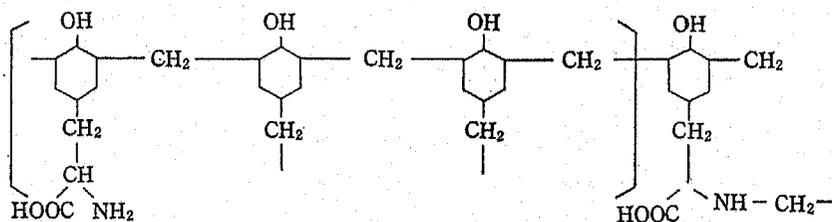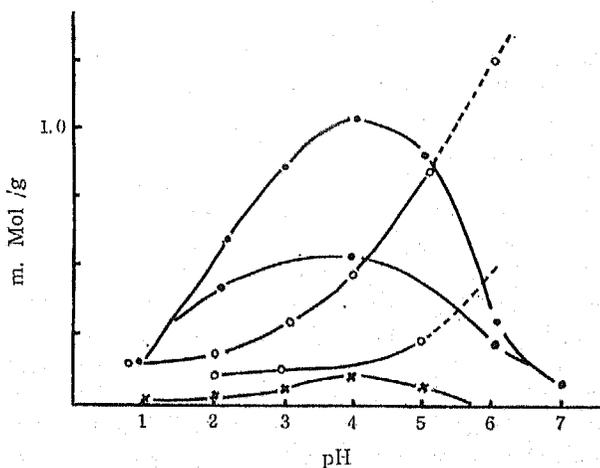
B. Chelate Resin
1. Phenylthiourea resin[11]

The property shown by many organic compounds of forming strongly coloured internal complexes with metals is put to good use in colorimetric analysis, being especially valueable when minute quantities of metal are to be determined. Frequently organic reagents show good selectivity. Most of organic reagents owe their selectivity to the chelate groups in them and most of these organic reagents have too complicate structure to be used in industry as a base of chelate resin. Among them, thiourea group seems to be excellent as chelating group in resin.

1) Synthesis of Phenylthiourea Resin

For preparation of selective adsorption resins, the follwing procedures are considered.

(1) Condensation of organic reagents with HCOH
(2) Condensation of organic reagents and Phenol or Resorcine with HCOH
(3) Introduction of chelate groups into polymers.

Phenylthiourea is known to have adsorbability to Cu, Au, Hg, Pd, Pt, Ag. Phenylthiourea was synthetized from Aniline hydrochloride and Ammomium thiocyanate. Phenylthiourea did not form good resin with HCOH in any acids or alkali solution. But it could be condensed with a cross linking agents such as phenol and resorcinol. Experiments were carried out under the same conditions as descibed in the case of Tyrosin resin.

2) Adsorption of Metals

The resin which was prepared from 20 g of Phenylthiourea, 80 ml of 35% HCOH, 15 g of Resorcine and NaOH catalyser was used for experiments. The amount absorbed was calculated from differences in the initial and final concentrations of the metal ion using Shimazu Photometric colorimeter. The metals used included Cu, determined by the use fo Na–diethyldithiocarbamate, Fe, o–phenanthroline, Co, ammonium thiocyanate. The shape of the curve was different in each case. Cu had the maximum at a lower pH value than any other metals. The slope of the curve of iron of this resin resembles that of o–aminophenol resin. Cu was absorbed from the solution containing Cu and Fe at pH 2.0 without any absorption of iron. Co may be separated from the solution of Co and Fe. The resin absorbed Cu far better than Co and Fe at pH 2.

II. 3–Hydroxyphenylthiourea Resin[12]

Phenylthiourea has thiourea group which shows a good selective adsorbability, but it is slightly soluble in water and was condensed only with resorcinol. Therefore it was sometimes difficult to obtain a good resin. Having OH

Fig. 3 Infra–red Spcetra of 3–Hydroxyphenylthiourea

Wave Length   Microns
A   Paraffin
B   3-Hydroxyphenylthiourea + Paraffin
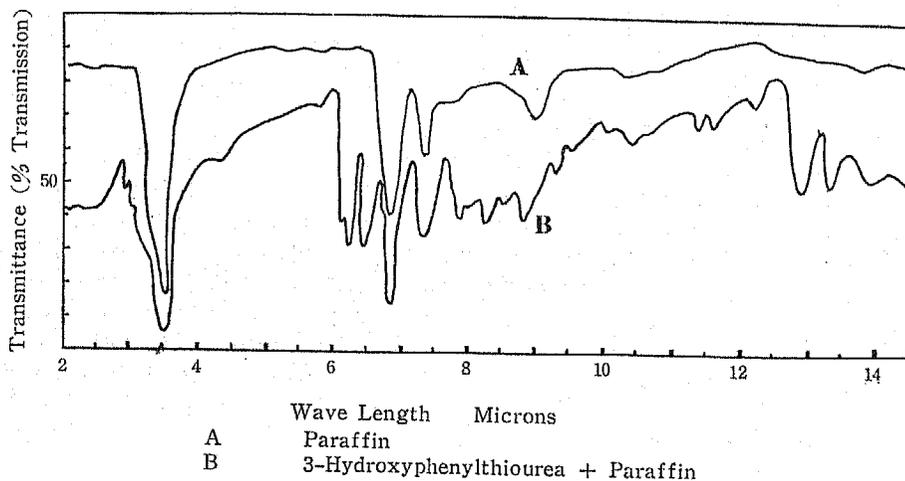
group, 3–Hydroxyphenyl thiourea was easily condensed with phenol to give a
good resin. The same selective adsorbability as Phenylthiourea is expected
to this resin. 3–Hydroxyphenylthiourea was obtained from m–aminophenol
hydrochloride and ammonium thiocyanate and recrystallization of it was
repeated from hot aqueous solution. Infrared–spectra were shown in Fig. 3.
Perkin–Elmer Model 21 infrared spectrophotometer was used here. $C_7H_8N_2OS$
M. P. 183–184°C

    Anal. calcd. for $C_7H_8N_2OS$: C 49.90 H 4.77 N 16.71
         found   : C 49.78 H 5.33 N 16.91

1) Preparation of 3–Hydroxyphenylthiourea Phenol resin

    17g of NaOH, 36 g. of 3–Hydroxyphenylthiourea (3HPTU) and 16 g. of
phenol were dissolved in I l of water. The mixture was heated with 120 ml. of
37% HCOH on water bath. About 100–110g of reddish black resin which was
chemically stable and mechanical strong resin was obtained. The conditioning
was done as in the case of Tyrosin resin.

2) Determination of chelate formation[13]

    Among the methods of determining the presence of chelates, the method
of using pH effect seems to be excellent. All metal chelates may be considered
as formed by the displacement of one or more usually weak acidic protons
of the chelating agent by a metal ion. Thus the addition of 3 HPTU to the
solution of metallic salts, such as Cu, Hg, Ag, causes a drop in the pH
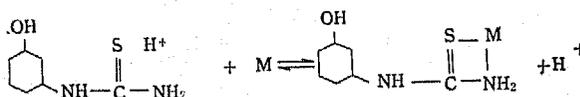
In a qualitative sense, the greater the tendency for metals to combine with
a given chelating agent, the greater the drop in pH. The pH titration curves
for 3 HPTU in the presence of various metal ions showed that Ag, Cu, Hg,
Pt formed chelate with 3 HPTU and Si, Li, Cu, Sr, Co did not. It may
be expected that chelate formation in resin results in a pH drop as in the
case of monomeric 3 HPTU. Therefore, the pH titration curves for 3 HPTU–
phenol were determined. Addition of Ag, Pt, Cu, Hg to resin caused pH
drop and addition of Ni did not as before (Fig. 4 and Fig. 5). The results
of these pH titration curves were confirmed by the results of adsorption
tests. In a qualitative sense, the pH drop in the case of resin was smaller
than that in the case of monomeric 3 HPTU. This is probably due to the
difficulty in forming the 2nd and 3rd chelate ring in resin. The chelate stability
will decrease owing to the steric hindrance, straine, and the decrease of
resonance in resin.

3) Adsorption of metal ions by 3 HPTU resin. [12]

    Following the method mentioned in the case of Tyrosin resin, I determined
the absorption of Hg, Pt, Cu, Ni, by 3 HPTU resin in various pH solutions.

Fig. 4 pH Titration Curves of 3 Hydro-
   xyphenylthiourea   Phenol   Resin   0.5g.
   resin, 2 M. KCl 20 ml, 0.1 N. KOH, OH,
   Total Solution 40 ml. ✕ Ni, ● Hg, ▲ Cu,
   △ Cu(without KCl), ◑ Pt
   0.5 g. Resin, 2 M KCl 20 ml, 0.05 M.
   Metal Solution 2 ml. ,0.1 N. KOH, HO, Total
   Solution 40 ml.
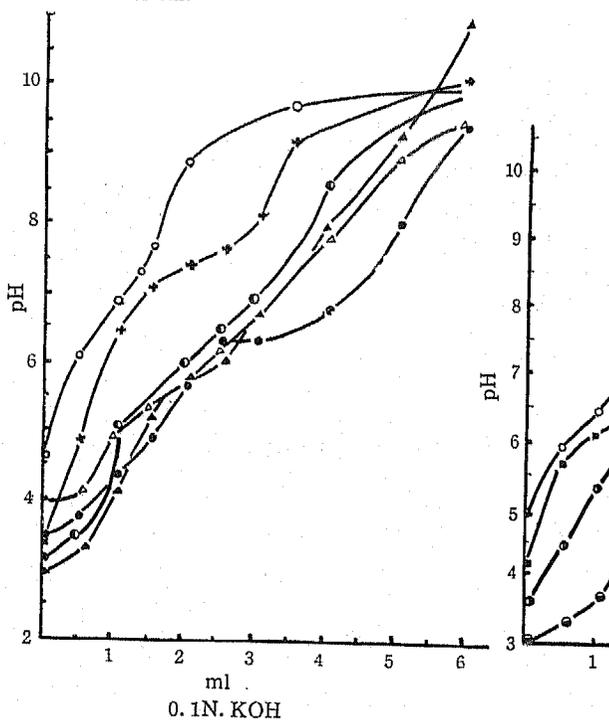
Fig. 5 pH Titration Curve of 3-Hydro-
   xyphenylthiourea Phenol Resin
            (Bottle Method)
         same as in Fig. 4
   ○ Pd, ▣ Ag, ◒ Au
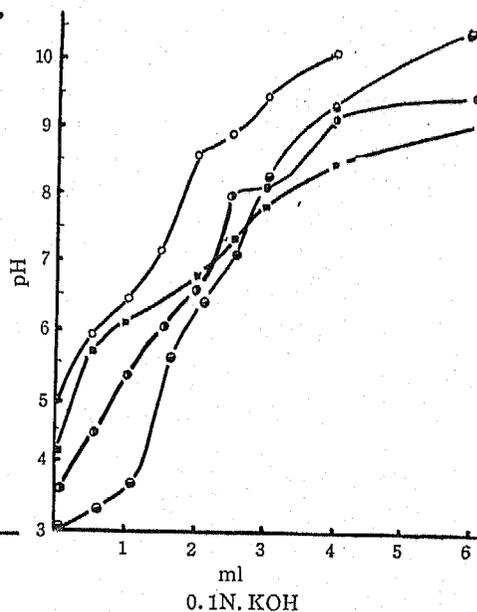
Structure of 3 HPTU resin:

Unit structure for 3 HPTU resin was expected as follows
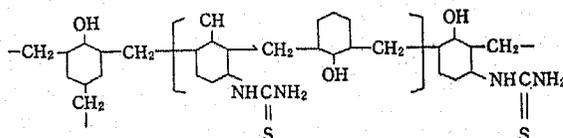
From above structure, theoretical maximum adsorbabilty was 3.45 m. mol/g.
resin. But Hg was absorbed only 1.77 m. mol/g. resin at pH in resin. This
shows that only one chelate ring is formed for one metal ion, however a
higher coordination number a metal ion may have, I think.

4) Effect of OH group in Phenolic Resin upon chelate Formation[14]

    Not only 3 HPTU but also phenol has OH group, OH group will be brought
in these polymers. Complex or chelate formation with OH group in these
resins may be considered. In order to know if the OH groups in phenol type
resin actually form complex or chelate, or not, pH titration curves for

Fig. 6 pH Titration Curve of Phenol Resin
            (Bottle Method)
○0. 5 g. Phenol Resin
△Cu Solution 0.05M 2 ml.
⊘0. 5g Phenol Resin Cu Solution Composition
  is the same as in the case of 3-Hydroxy-
 phenylthiourea-Phenol resin
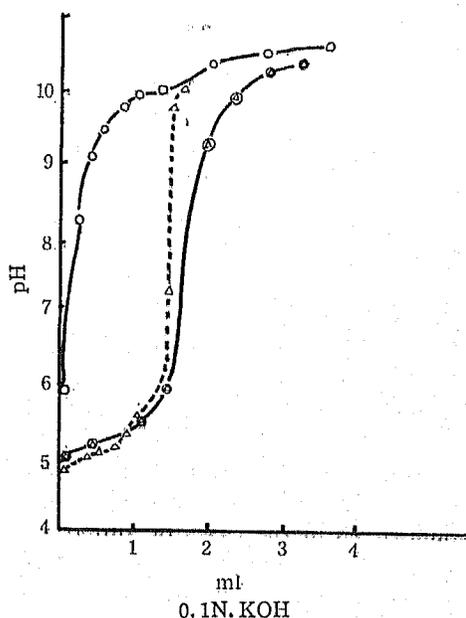
Fig. 7 Adsorption of Metal Ions by 3-
  Hydroxyphenyl thiourea Resin
△Cu, ×Ni 0. 5m, Mol in 30 ml /0. 5g. resin
●Hg   2 m. Mol in 60 ml /0. 5g, resin
◑Pt   0. 16 m. Mol in 30 ml /0. 1g. Resin
◒Au   0. 3 m. Mol in 30 ml /0. 25 g. Resin
○Pd   0. 1m. Mol in 30 ml /0. 25g. Resin
▧Ag   1 m. Mol in 60 ml/0. 25g. Resin
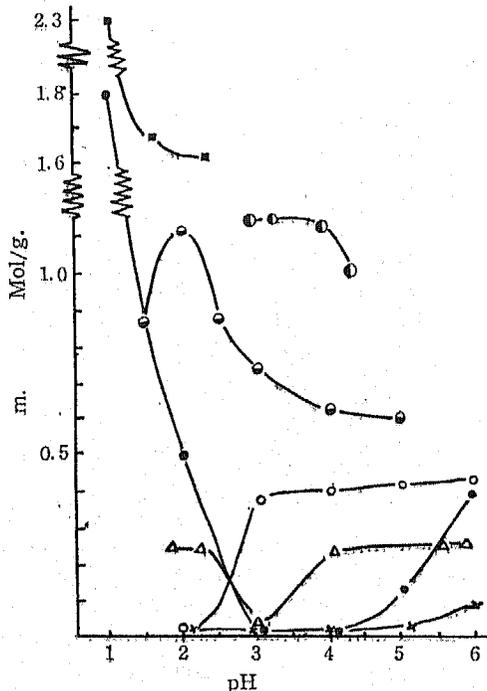
phenol resin in the presence of Cu and Hg were determined. The initial part
of pH titration curves of Cu metal and of phenol resin in the presence of
Cu were overlapped each other, This shows that pH drop in this case
is not due to complex formation. So, the pH drop in 3 HPTU resin in
the presence of Hg, Cu, Pd, Pt, Ag, Au were mainly attributed to chelate
formation,

5) Adsorption of Ag on 3 HPTU resin under vaious conditions
     Adsorption of metals by chelate resins is greatly affected by the conditions.
Adsorption tests were again attempted. The results were summarized in table 4.
Making a comparison between A and B, we could realize that adsorption
of Ag increased with concentration of Ag. From the results of B and C,
adsorption of Ag was not decreased even in the presence of a large quantity
of K. E was done under the same condition as D except the addition of HNO_3
to D. In stead of 3 HPTU resin, p-phenolsulphonic acid resin was used to
compare adsorbability under the same condition as B. The results showed
that adsorption of Ag by p-phenol sulphonic acid resin was greatly decreased.

Table 4   Adsorption of Ag under various conditions.

Sample	Absorbed Ag/g. Resin	Absorbed Ag/TotalAg %	Concent-ration of Ag m. mol/1	Solution Contact with resin ml/g	Total Ag m. Mol/g resin	pH of Solution	Mol Ratio K/Ag
A1	0.67	52	0.013	80	1	1.32	—
A2	0.49	37.8	0.006	160	1	1.18	—
A3	0.41	31.5	0.004	240	1	1.18	—
B1	0.88	34.0	0.025	80	2	1.4	—
B2	0.71	27.3	0.013	160	2	1.35	—
B3	0.67	26.0	0.008	240	2	1.44	—
C1	0.81	32.0	0.025	80	2	1.12	40
C2	0.71	27.3	0.013	160	2	1.14	40
C3	0.66	25.3	0.008	240	2	1.15	40
D1	0.57	43.9	0.013	80	1	1.99	—
D2	0.61	23.2	0.013	160	2	1.81	—
D3	0.86	16.7	0.013	240	4	1.99	—
E1	0.68	26.3	0.025	80	2	2.92	—
E2	0.49	19.1	0.013	160	2	2.41	—
E3	0.39	15.0	0.008	240	2	2.42	—
F1	0.28	14.0	0.025	80	2		—
F2	0.04	2.0	0.025	80	2		20

When minute quantity of Ag is present, pH drop is so small that it is difficult to realize chelate formation by pH titration curve. The prolonged curing of 3 HPTU resin bring it to breakdown, as in the cases of amino acid resins which have a projecting chelate group. The formation of a closed net structure by curing makes it impossible to include such a projecting group as thiourea.

III.   Mercaptobenzthiazol Resin[15]

In order to determine chelate or complex formation, precipitation test can be used in a qualitative sense. This test is simple but not so reliable that the results of pH titration curve and adsorption spectrophotometry were compared with precipitation tests. It does not always follow that all metals precipitating with compounds do form chelate. Thus, for example 3 Hydro-xyphenylurea has a similar structure as 3 Hydroxyphenylthiourea, but preci-pitation test, pH titration curve, and ultravioletabsorption spectra show that it does not form precipitate nor chlate. Oxygen in urea group has lone pair electron as Sulphur in thoiurea. The difference in chelate formation must be due to the difference between the diameters of sulphur and oxygen. Merca-ptobenzthiazol was recrystallized (M. p 177—179°C) and used for pH titration curve. The metals which cause large pH drop will combine simultaneously both S and O, while the metals which cause small pH drop will combine either with only S or N atom. 10 g of Mercaptobenzthiazol and 8.2 g of phenol were dissolved in 40 ml of the solution containing 8 g of NaOH. The mixture was reacted with HCOH on water bath, and the resin so formed was crushed
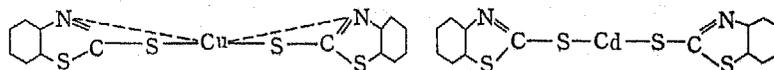
and heated at 90°C and then washed with water and conditioned for adsorption test. A cation exchange capacity of this resin was 1.81 m. eq./gr. The absorption capacity of this resin increased with the concentration of the metal ions. The shape of the curve is different in each case. So that this resin may be used for the separation of these metals. (Fig. 8)

Fig. 8 Adsorption of Metal Ions by Mercaptobenzthiazol Resin
     A   Hg 0.06 M (Total 2.22 m. Mol)   B   0.04 M. Hg (Total 1.11 m. Mol)
     C   Co 0.06 M (Total 1.69m. Mol)   D   0.025M. Co (Total 0.846m. Mol)
     E   Cd 0.025 M (Total 1.0m. Mol)
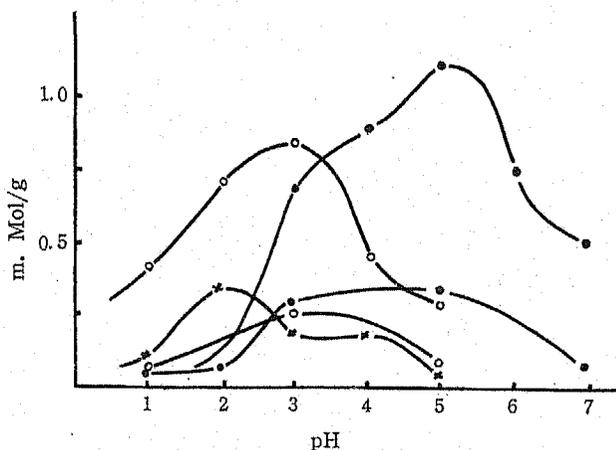
C. P–Hydroxyphenylarsonic acid resin[16]

Arsenic acids have been used as a special reagent to Ti, Zr, Th. Selective adsorptive resin to these metals can be prepared by introducing arsenic acid group in polymer.
1) Synthesis of Arsonic acid resin:
   synthesis tests were made under the following conditions
   (1) Synthesis of p–hydroxyphenylarsonic acid from phenol and arsenic acid.
   (2) p–hydroxyphenylarsonic acid + HCOH + NaOH catalyser
   (3) p–hydroxyphenylarsonic acid + Phenol + HCOH + NaOH catalyser
   (4) polyvinylalcohol + arsenic acid
Good resins were obtained in (2) and (3). These resins were not soluble in water, acids and alkali. Preparation of resin : I mole of p–hydroxyphenylarsonic acid is dissolved in the solution containing 2.5 mol of NaOH and add 3 mols of HCOH. Heat the mixture on water bath, crush and cure the resin at 95°C for 10 hrs. The copolymer made from 1 mol of p–hydroxyphenylarsonic acid and 1 mol of phenol was used for adsorption test.
2) Adsorption of Zr.

　　　p-hydroxyphenylarsonic acid HCOH resin and p-hydroxyphenylarsonic acid phenol HCOH resin were compared with polyvinyl alcohol arsenic acid ester on adsorbability of Zr ion in acid solution. These resin could adsorb Zr ion in a strong acid solution. The amount of largest adsorption is much smaller than we expected (0. 32–0. 43 m. mol /g resin). Under a certain condition, the pH titraion curve of p-hydroxyphenyl arsonic acid–resorcin resin showed that the quantity of the primary hydrogen decreaesed as compared with that of the second one during the condensation.

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