

A Chemical Eight Group Separation Method for Routine Use in Gamma Spectrometric Analysis

1. Ion exchange experiments.

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ROUTINE USE IN GAMMA SPECTROMETRIC ANALYSIS.

I. Ion exchange experiments.

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Summary:

A method for the separation of chemical elements in 8 groups suitable for gamma spectrometric analysis has been developed. One group of elements is separated by distillation during dissolution of the sample. The other groups are obtained by means of short ion exchange columns coupled in series.

An anion exchange column saturated with chloride ions separates chloride complexes, peroxides and other anions from a 3-n HCl + 0,3 % H_2O_2 sample solution.

Some of the chloride complexes are eluted with 0,1-n HCl + 0,3 % H_2O_2 and subsequently adsorbed as cations on a cation exchange column in hydrogen form. A few eluted elements which do not form cations in this case are found in the effluent.

Elements passing the anion exchange column in chloride form without adsorption are separated from a H_2O solution as citrate complexes, hydroxides, cations and hexametaphosphate complexes. This is done by coupling in series two anion exchange columns subsequently in citrate- and hydroxide form and followed by a cation exchanger in sodium form. A mixed bed column ends the series.

The behaviour in the separation series of most elements forming gamma emitting isotopes with halflives exceeding 10 minutes on irradiation with thermal neutrons has been studied.

The method has been used routinely for one year.

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A chemical eight group separation method for routine use in gamma spectrometric analysis.

1. Introduction.

During the last few years a number of successful chemical procedures for sequential analysis of radionuclide mixtures have been published (1, 2, 3, 4, 5).

The present method has been developed for routine use mainly in connection with gamma spectrometry of atomic reactor materials and biological samples. Experience has shown that it may also be valuable for analysis of a great variety of other materials.

The use of small anion exchange columns coupled in series for group separations of elements in water soluble samples has been described earlier (6). The same technique has been further developed for more general application to problems in gamma spectrometric analysis. The elements are separated in 8 groups. One group is obtained during dissolution of the irradiated samples which is performed with hot, strong hydrochloric - or sulphuric acid during addition of hydrogen peroxide. The halogens are driven off by this treatment after addition of carriers and absorbed in strong sodium hydroxide. The solution is measured directly with a multichannel gamma spectrometer. This conventional way of separating the halogens will not be described in further details. The three next groups of elements are obtained after dissolution of the sample in 3-n HCl + 0.3 % H_2O_2 . The solution is flowed through an anion exchange column in chloride form, which adsorbs chloride complexes, anions of strong acids and the peroxides of molybdenum and tungsten. This large amount of adsorbed elements is split into three groups by elution of some of the chloride complexes with 0, 1-n HCl + 0, 3 % H_2O_2 . The eluted elements are partly adsorbed on a cation exchanger in hydrogen form, which is coupled in series with the chloride form during the elution. The rest remains in the effluent.

The 3-n HCl + 0,3 % H_2O_2 effluent from the chloride form is evaporated to dryness. The residue is dissolved in weak HCl and titrated with NaOH against methyl orange as indicator. This solution is passed through four ion exchange columns coupled in series. The first two columns are anion exchangers subsequently in citrate- and hydroxide form. The third one is a cation exchanger in sodium form. A mixed bed column prepared from equal amounts of a cation exchanger in hydrogen form and an anion exchanger in hydroxide form ends the series. The anion exchangers separate elements forming citrate complexes or sparingly soluble hydroxides. The cation exchanger adsorbs the alkalies and alkaline earths, which are the only elements passing through the preceding anion exchangers. The alkaline earths are eluted with a solution of hexametaphosphate and subsequently again adsorbed on the mixed bed column ending the series.

The activity of the resin columns is mostly measured directly with a multichannel gamma spectrometer.

2. Experimental.

2.1. Resin forms.

The preparation of the different resin forms is described in detail in the second part of this paper. Dowex 2 x 10, 200 - 400 mesh was used as anion exchange resin and Dowex 50 W x 12, 200 - 400 mesh as cation exchange resin.

The prepared resin forms were kept on stock under distilled water during the experiments.

2.2. Ion exchange columns.

Pyrex sintered glass filter crucibles of common type, 2,2 cm diam., 4,5 cm height were filled with the appropriate resin forms to 2,7 cm height (10 ml wet resin) by means of suction. The chloride form was washed with a small portion of 3 n HCl. The others were washed with distilled water. The cation exchange column used for the adsorption of eluted chloride complexes was 2 cm in diam. and 6,5 cm in height.

2.3. Apparatus.

The only apparatus used for the experiments consisted of a 100 ml suction flask connected to a rubber ball for the application of suction. A test tube placed inside the flask gathered effluent and washing fractions.

2.4. Sample preparation and separation.

2.4.1. Irradiation and dissolution.

The experiments were performed with elements or salts of elements of Pro analysi grade. Amounts from 0,001 - to 3 mg were irradiated with a thermal flux of about 10^{12} n/cm² sec. from 10 minutes to 5 days, depending on halflives.

The irradiated samples were mostly dissolved in 5 ml hot 1:1 HCl containing 0,5 ml 30 % H₂O₂ and taken to dryness on a water bath. Subsequently they were dissolved and diluted to a suitable strength of gamma activity with 3 n HCl + 0,3 % H₂O₂ (1 ml 30 % H₂O₂ per 100 ml solution). Carriers were not added.

2.4.2. Dowex 2, chloride column.

For each element studied a 5 ml aliquot of the 3-n HCl + 0,3 % H₂O₂ stock solution was passed through the anion exchange column in chloride form at a rate of about 4 ml/min. A faint suction was applied by means of the attached rubber ball. After the dropping had ceased the column was washed with 1,5 ml portions of 3-n HCl + 0,3 % H₂O₂ at the same rate. The effluent and three washing fractions of 3 x 1,5 ml each were gathered separately and diluted to 10 ml with water. The activity of these samples was compared with the activity of the drained and homogenized resin at definite geometry with the gamma spectrometer. Table 1, column 3 shows the per cent activity adsorbed on the resin after washing with 9 x 1,5 ml of 3-n HCl + 0,3 % H₂O₂.

2.4.3. Elution of chloride complexes.

Elution of some of the chloride complexes adsorbed on the Dowex 2, chloride column was done with 400 ml 0, 1-n HCl containing 0, 3 % H_2O_2 . After adsorption of a certain element the column was coupled in series with a cation exchange column, 2 cm diam., 6, 5 cm height and the solution sucked through at a rate of 15 - 20 ml/min. The resin masses were separately homogenized after dilution of the chloride form to 20 ml with unused anion exchange resin and their activities compared with the gamma spectrometer. The per cent activity remaining on the chloride form was calculated, and the results are given in Table 1, column 4.

In some cases the effluent from the cation exchanger was evaporated down to 20 ml and controlled for possible radioactivity. Thus it was found that eluted arsenic, antimony and selenium quantitatively passed through the cation exchanger together with 75 per cent of the tellurium activity. These elements may be determined in the effluent.

2.4.4. Dowex 2, citrate column.

Elements showing incomplete adsorption on the Dowex 2, chloride form were studied in a quite analogic manner on a Dowex 2, citrate column. The effluent and the washing fractions from the chloride form were evaporated to dryness on a waterbath. The residue was dissolved in 5 ml distilled water, pH \approx 4, 2, and the solution passed through the citrate column. The column was washed with 9 x 1, 5 ml of distilled water. The results from these experiments are given in Table 1, column 5.

2.4.5. Dowex 2, hydroxide column.

The radioactive effluent and washing fractions for elements passing the citrate form without complete adsorption were flowed without pretreatment through a similar column in the hydroxide form. The column was washed with 9 x 1, 5 ml 0, 01-n NaOH, Table 1, column 6.

2.4.6. Dowex 50, sodium column.

Effluent and washing fractions from the hydroxide form contain only the alkalies and alkaline earths. This solution was passed through a Dowex 50, sodium column, Table 1, column 7.

2.4.7. Elution of hexametaphosphate complexes.

Elution of the alkaline earths, which together with the alkalies were adsorbed on the Dowex 50, sodium column, was done with 20 ml 0,1-n NaOH containing 600 mg sodium hexametaphosphate. The solution was continuously flowed through the column at a rate of about 4 ml/min. Table 1, column 8.

2.4.8. Measuring technique.

The experiments were carried out with strong activities allowing mostly a distance of 10 cm between sample and detector. The detector consisted of a 3" x 3" sodium iodide crystal.

Complete gamma spectrograms were plotted for about 2/3 of the studied elements, and the activity calculated as the area of the principal photo peak. For the rest of the elements the activity studied was so dominant that corrections for impurities could be omitted (e.g. Mn, As, Cu, La, Ga, W). In these cases only the total gamma activity was registered. All measurements were corrected for coincidence and background. No corrections were done for different gamma absorption in wet resin and liquid samples.

3. Results and discussion.

3.1. Dissolution of samples.

The mixture of hot strong HCl and H_2O_2 is very efficient for the dissolution of a great variety of samples. In addition this solution will probably, independent of initial oxidation state, bring manganese to the divalent- and chromium to the trivalent state. This makes possible a quantitative separation of the very often strong activities from these elements on the hydroxide form in the separation series. The possible

influence on the separation of the initial oxidation states of the elements shown in Table 1 has been studied in some details only for chromium, manganese and ruthenium. However, one years practical experience with the group separation method has so far shown no discrepancies from the values given in Table 1.

Some few elements or compounds of elements which are practically insoluble in the $\text{HCl} - \text{H}_2\text{O}_2$ mixture, were initially brought into solution in other media like aqua regia or $\text{H}_2\text{SO}_4 - \text{HF}$ mixtures, taken to dryness and then treated with $\text{HCl} - \text{H}_2\text{O}_2$. In the case of tantalum, which hydrolyzes in $\text{HCl} - \text{H}_2\text{O}_2$, filtration through a 4 G sintered glass filter was done. The filtrate was used for the experiments.

The dissolution of zirconium and hafnium in water after evaporation to dryness of the $\text{HCl} - \text{H}_2\text{O}_2$ solution was done after addition of a trace amount of citric acid to the solution during the evaporation.

3.2. Adsorption of chloride complexes.

A comprehensive study of anion exchange separations of chloride complexes from hydrochloric acid solutions has been done by Kraus and Nelson (7).

In the present work 3 n HCl solutions were chosen because this acid strength is advantageous for the separation of many elements important in reactor technology. For example, experience showed that 3 n HCl is the lowest possible acid strength for a near to 100 per cent adsorption of iron, gallium and antimony on the Dowex 2, chloride column, and it is the highest one for complete passage of cobalt and chromium. A small adsorption of manganese was observed from HCl solutions above 5 n. An easily detectable adsorption of Cu starts at HCl concentrations somewhat above 1 n.

The use of small amounts of H_2O_2 in the 3 n HCl sample solution was found necessary for the quantitative adsorption as peroxides of

tungsten and molybdenum. Also the 0,1 n HCl elutriant for chloride complexes must contain H_2O_2 to avoid elution of large amounts of these two elements. It should be mentioned that relatively strong activities from tungsten or molybdenum are very often met with in practical gamma spectrometric analysis of reactor materials and biological materials. By omitting the use of H_2O_2 in sample solution and elutriant these activities would be distributed into three different groups in the separation series, and thus unnecessarily mask the activities of many other elements.

3.3. Elution of chloride complexes.

0,1-n HCl was found to be the best elutriant for many chloride complexes. The quantitative elution of elements like iron and gallium is difficult with weaker acid strengths or water. This is probably due to the precipitation of the corresponding hydroxides by the strongly basic Dowex 2 resin. In addition, 0,1-n HCl is sufficiently strong to leave cadmium, an important element in reactor technology, uneluted on the chloride column, thus enabling the separate elution of this element with water afterwards (7).

3.4. Separation of citrate complexes and hydroxides.

The separation of citrate complexes and hydroxides has been discussed earlier (6). In the present work only a few details like column heights and washing procedures have been somewhat changed. Also the studies have been expanded to incorporate a larger amount of elements.

One main reason for changing column heights and washing procedures is some practical problems met with in gamma spectrometry of e.g. biological samples. In this case enormous amounts of Na-24 activity have to be completely washed out of the columns without affecting the adsorbed trace elements. This was not possible with the first procedure.

3.5. Separation of hexametaphosphates.

The separation of the alkaline earth metals from the alkalies is desirable in gamma spectrometry of e.g. uranium fission products, some biological samples etc.

After an initial adsorption of these two groups of elements on a short cation exchange column in sodium form the alkaline earths may be easily eluted with a dilute, alkaline solution of sodium hexameta-phosphate. The method was in one case tried out for solutions containing only trace amounts of irradiated salts of either Ca, Sr or Ba, as shown in Table 1. In another case 5 mg of the appropriate cation was added as carrier. In both cases a complete elution of the alkaline earths was obtained.

3.6. Table 1.

Only the results found after washing of the columns with 9 x 1,5 ml of the respective washing solutions are given. Measurements, which were also carried out at the intervals 3 x 1,5 and 6 x 1,5 ml of washing solution, showed that 9 x 1,5 ml is preferable for gamma spectrometric analysis.

The error of the given results has not been especially studied. However, it may in no cases be greater than 3 % of the total activity.

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Table 1.

1. Irridated material	2. Isotope measured	% activity. Error < 3 % of total activity.					
		3. Dowex 2, chloride	4. Dowex 2, chloride after elution	5. Dowex 2, citrate	6. Dowex 2, hydroxide	7. Dowex 50, sodium	8. Dowex 50, sodium after elution
NaCl	Na-24	0	-	0	0	100	100
MgSO ₄	Mg-27	0	-	3-7	0	93-97	-
KCl	K-42	0	-	0	0	100	100
CaCl ₂	Ca-47	0	-	0	0	100	1, 1
Sc ₂ O ₃	Sc-46	0, 1	-	100	-	-	-
CrCl ₃	Cr-51	0, 1	-	0, 8	99, 1	-	-
(NH ₄) ₂ CrO ₄	Cr-51	0	-	1, 2	98, 8	-	-
MnSO ₄	Mn-56	0	-	1, 4	98, 6	-	-
MnO ₂	Mn-56	0	-	1, 4	98, 6	-	-
FeSO ₄	Fe-59	99, 0	0	-	-	-	-
Co(NO ₃) ₂	Co-60	0, 2	-	99, 8	-	-	-
NiSO ₄	Ni-65	0	-	100	-	-	-
CuSO ₄	Cu-64	55-65	0	35-45	-	-	-
ZnSO ₄	Zn-65	100	0	-	-	-	-
Ga, metal	Ga-72	98, 2	0	-	-	-	-
As ₂ O ₃	As-76	15-25	0	75-85	-	-	-
Se, gray	Se-75	10-20	0	80-90	-	-	-
RbCl	Rb-86	0	-	0	0	100	100
SrCl ₂	Sr-87	0	-	0	0	100	0

ZrOCl ₂	Zr-95	0	-	100	-	-	-
ZrOCl ₂	Nb-95	0	-	100	-	-	-
Mo, metal	Mo-99	100	100	-	-	-	-
Mo, metal	Tc-99	100	100	-	-	-	-
Ru, metal	Ru-103	100	99, 5	-	-	-	-
Uranium	Ru-106, Rh-106	96, 4	96, 4	-	-	-	-
AgNO ₃	Ag-110	100	100	-	-	-	-
CdO	Cd-115	100	100	-	-	-	-
CdO	In-115	100	0	-	-	-	-
In, metal	In-114	100	0	-	-	-	-
Sb ₂ O ₃	Sb-122	97, 9	3, 3	-	-	-	-
Te, metal	Te-131	100	0	-	-	-	-
CsCl	Cs-134	0	-	0	0	100	100
BaCl ₂	Ba-131	0	-	0	0	100	0
La(NO ₃) ₃	La-140	0, 6	-	99, 4	-	-	-
Ce ₂ (SO ₄) ₃	Ce-141	1, 2	-	98, 8	-	-	-
HfO ₂	Hf-181	0, 4	-	99, 6	-	-	-
Ta ₂ O ₅	Ta-182	0-5	-	95-100	-	-	-
W, metal	W-187	100	100	-	-	-	-
Re, metal	Re-186	100	100	-	-	-	-
Os, metal	Os-193	100	100	-	-	-	-
Ir, metal	Ir-192	98, 3	98, 3	-	-	-	-
Au, metal	Au-198	100	100	-	-	-	-
HgSO ₄	Hg-197	100	100	-	-	-	-
UO ₂ (NO ₃) ₂	U-239	100	-	-	-	-	-
UO ₂ (NO ₃) ₂	Np-239	0	-	80-90	10-20	-	-

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