A Group Separation Method for Gamma Spectrometry of Complex Radionuclide Mixtures — with Special Application to Stainless Steel and its Corrosion Products

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Short anion exchange columns coupled in series and saturated with chloride, citrate and hydroxide ions have been used for simple and very rapid separations of common elements in water solutions as a pretreatment for subsequent analysis with gamma spectrometry. A method was developed for the analysis of stainless steel, its corrosion products, and other elements, present as impurities in a water cooled nuclear reactor. Practical examples are described in detail.

With this method it seems possible to measure continuously water corrosion rates of individual or small groups of stainless steel elements.

Since the use of scintillation counters for gamma radiation was originally described by Bell and Cassidy¹, it has been shown that gamma spectrometry makes possible the identification and quantitative determination of gamma emitters in mixtures of radionuclides^{2,3}.

As most elements form radioactive gamma emitting isotopes on irradiation with thermal neutrons in an atomic reactor, gamma spectrometry has become a modern analytical tool of increasing importance.

Gamma spectrometric analysis of simple radionuclide mixtures can in many cases be carried out successfully without prior chemical separation of individual constituents. However, a coarse separation of the present elements in groups is often necessary or preferable. The presence in a sample of only minute amounts of common elements with extremely high activation cross section and hard gamma radiation, like sodium and manganese, giving rise to $^{24}_{11}\text{Na}$ and $^{56}_{25}\text{Mn}$, can by Compton distribution partly or completely mask the activity of other elements. In many analyses the alkalies and alkaline earths constitute only interfering impurities without interest. A rapid and accurate anion exchange method for separating them from, as it seems, all other elements has been worked out. The method simultaneously allows the latter elements to be gathered in groups suitable for gamma spectrometry.

Samuelson and Schram ⁴ used an anion exchange column (as citrate) for separating alkali salts from various cations in a water solution. The use of anion exchange resins as solid precipitants and filters was suggested by Glueckauf and Roberts ⁵. The present method makes use of these principles. The behaviour of different cations has been studied by flowing neutral water solutions through short anion exchange columns in the citrate- and the hydroxide form. An anion exchanger in the chloride form was also studied, in as much as metals like tungsten and molybdenum can be easily separated from many other elements as negatively charged ions by the chloride form after an initial HCl-H₂O₂ standard treatment of irradiated samples.

EXPERIMENTAL

The experiments were performed with irradiated metallic chromium, molybdenum and tungsten, and furthermore salts of the cations, Na⁺, Mn²⁺, Fe²⁺, Co²⁺, Ni²⁺, Cu⁺, Zn²⁺ and Sr²⁺. The samples were individually brought into solution with hot 1:1 HCl containing a few drops of H₂O₂ and taken to dryness on a water bath. Subsequently they were dissolved in water and diluted to a suitable strength of gamma activity. Carriers were added in amounts of about 5 mg of the appropriate cation per 100 ml of solution. No carriers were added to the solutions of tungsten and molybdenum. Then 20 ml portions of a single gamma emitter solution were added to four ion exchange columns consisting of Dowex 2, 200–400 mesh in the citrate, chloride- and hydroxide form, and Dowex 50, 200–400 mesh in the hydrogen form. Each column consisted of 10 ml in water sedimented resin contained in a 2.5 cm diameter glass filter crucible. The active solutions were sucked through at a rate of about 4 ml/min and the columns washed with two five ml portions of water and drained by suction. Finally the crucibles were placed directly at definite geometry on the top of a gamma scintillation detector, and the activity assayed with a single channel pulse analyzer.

The activity of the Dowex 50 resin was measured and used as a standard for the estimation of the per cent absorption on the others. The eluate was controlled for possible gamma activity.

RESULTS AND DISCUSSION

The behaviour of the different ions on the ion exchange columns is summarized in Table 1.

The first column of the table illustrates the oxidation states of the elements after the initial HCl-H₂O₂ treatment.

The behaviour of hydrogen peroxide in acid medium can be advantageously utilized for the analysis of stainless steel elements, which is shown by a practical example further on. Besides its powerful solving and oxidizing action on many elements it will for example reduce possible higher valences of manganese to the divalent state and does not effect oxidation of trivalent chromium in hydrochloric acid. As a result chromium, if not initially present as chromate, and manganese can easily be quantitatively separated from other elements.

The molybdates and tungstates obtained by solution of the metals consist of many complicated compounds which do not seem to be very well known. Their partly retention on the Dowex 50 resin is probably due to the precipitation of the corresponding acids, as additional experiments showed that they were not or only to a very small extent adsorbed on a cation exchanger in Na⁺ form.

Table 1.

Cation	% adsorption		Error < 5 %	
	Dowex 2 chloride	Dowex 2 citrate	Dowex 2 hydroxide	Dowex 50 hydrogen
Na ⁺	0	0	0	100
Mn ²⁺	0	0	100	100
Fe ²⁺	0	100	100	100
Co ²⁺	0	100	100	100
Ni ²⁺	0	100	100	100
Cu ²⁺	0	100	100	100
Zn ²⁺	0	50–70	100	100
Sr ²⁺	0	0	0	100
Cr ³⁺	0	0	100	100
Molybdates	100	100	100	30–70
Tungstates	100	100	100	30–70

The retention of Zn²⁺ on the citrate form was found to be 90 % if the final washing procedure with two 5 ml portions of water was omitted. Washing with about 100 ml of water caused a quantitative break through of the zinc activity.

PRACTICAL EXAMPLES

1. Stainless steel analysis

According to Table 1 a separation into three groups of common steel components is achieved by passing a water solution of the irradiated sample through three Dowex 2 columns subsequently in chloride-, citrate- and hydroxide form. Molybdenum and tungsten are quantitatively retained on the chloride form. Other elements pass through to the citrate resin, where iron, cobalt and nickel are adsorbed as complexed ions. Manganese and chromium, however, still pass through and are finally precipitated on the hydroxide form.

The practical arrangement is shown in Fig. 1. It consists of three identical glass filter crucibles attached to each other and to a suction flask by means of rubber rings.

Carriers of Ni²⁺, Co²⁺, Mn²⁺ and Cr³⁺ are added to the sample solution. An even flow rate of the active solution is obtained if the crucibles are filled with water before being attached to each other.

After drainage of the active solution the upper crucible is washed with water and removed for counting. The next one is then drained and treated in the same way, and so on.

Separation speed. The various resin forms are kept on stock under distilled water, and the whole separation procedure is finished about one hour after removal of the sample from the pile. The gamma spectrometric measurements of the first resin column in the series can start about 20 min earlier. However, a few experiments with stainless steel has been carried out by converting the sample to water soluble sulphates with a H₂SO₄-H₂O₂ treatment before irradiation.

Fig. 1.

tion. The active material was directly dissolved in water and passed through the resin columns. The activity measurements could then start about 10 min after the end of irradiation. In this way it may be possible to analyze elements with short lived isotopes, like vanadium in steel and magnesium in aluminium alloys. However, the possible interfering influence on the separation of Szilard-Chalmers reactions has not been studied in detail.

Gamma spectrometric measurements. The single channel pulse analyzer used for the analysis has previously been standardized against known amounts of the various elements. The measurements are carried out in the usual way by writing spectra and following decays.

The separation procedure as now described is, however, not ideal for the gamma spectrometry of cobalt-containing steel. Because of the similar gamma radiation emitted from $^{60}_{27}Co$ and $^{59}_{26}Fe$, which both are retained on the citrate form of the resin, their individual determination is difficult. The problem can, however, be easily solved by eluting the resin, extracting the iron with ether and again adsorbing the cobalt activity on an ion exchanger for comparative measurements.

The determination of small amounts of molybdenum in the presence of tungsten is best done after some days decay of the 24 hours $^{187}_{74}W$. Chromium in the presence of manganese is easily determined about one day after the end of irradiation.

2. Corrosion measurements

Some measurements of corrosion products in the heavy water of the Swedish R1 reactor has been carried out. 20 ml portions of D_2O were passed without pretreatment and addition of carriers through the same arrangement of resin

forms as used for the steel analysis, except that an additional Dowex 50 column in the hydrogen form was coupled after the resin in the hydroxide form for the control of the adsorption efficiency of the others.

About 20 ml of each resin form were used and the D₂O samples passed through at a rate of about 3 ml/min, owing to the extremely small salt concentration in the heavy water, which is continuously demineralized in the external reactor system.

The measurements started 30 min after the end of irradiation. $^{187}_{74}\text{W}$ was found only on the chloride form and $^{56}_{25}\text{Mn}$ on the hydroxide form, just as in steel analysis. $^{64}_{29}\text{Cu}$ had been quantitatively retained on the citrate form. The cation exchanger, ending the series, showed only a clean $^{24}_{11}\text{Na}$ spectrum. The eluate was inactive. Although in all cases the separation of various elements seemed to be quantitative, this is difficult to state definitely, due to the very small amounts of activities present in a sample. However, there is reason to believe that the separation method described may be of some value for the continuous control of individual- or groups of water corrosion products in a nuclear reactor, and for material testing experiments.

CONCLUSIONS

From the practical examples given, in addition to a lot of other cases, it appears that the present group separation method used in connection with gamma spectrometry, is very helpful for the identification and quantitative determination of many elements. Because of the simplicity of the method, and also its rapidity it has been adopted as a routine procedure in this laboratory. However, it may also exist many possibilities to prepare the anion exchange resin in other forms, *e.g.* sulphide, sulphate, carbonate, fluoride *etc.* to allow more advantageous separations in many practical cases.

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