RAPID CONTINUOUS CHEMICAL METHODS FOR STUDIES OF NUCLEI FAR FROM STABILITY

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Abstract

Fast continuous separation methods accomplished by combining a gas-jet recoil-transport system with a variety of chemical systems are described. Procedures for the isolation of individual elements from fission product mixtures with the multistage solvent extraction facility SISAK are presented. Thermochromatography in connection with a gas-jet has been studied as a technique for on-line separation of volatile fission halides. Based on chemical reactions in a gas-jet system itself separation procedures for tellurium, selenium and germanium from fission products have been worked out. All the continuous chemical methods can be performed within a few seconds. The application of such procedures to the investigation of nuclides far from the line of p-stability is illustrated by a few examples.

1. Introduction

Though extensive efforts have been made in the last years to study nuclei far from the region of p-stability, there are still many nuclides which remain to be discovered or whose decay properties are of interest but not known well enough. For the isolation of such short-lived nuclides from complex reaction product mixtures mainly mass separation1 or chemical procedures2 are suited. Most recent progress in both methods is due to developments and improvements of on-line separation techniques. The use of conventional mass separators with the advantage of a rapid and unambiguous isobaric separation is limited to elements for which suitable target-ion-source systems are available; e.g. non-volatile elements like Zr and Nb have low yields or are inaccessible by this method. Therefore, the emphasis in developing continuous chemical separation procedures, which are selective with respect to the atomic number, was put on those elements which cause problems in ISOL-systems.

On-line chemical separations can be accomplished by combining a gas-jet recoil-transport system3 with a variety of separation steps. The present paper describes its combination with the multistage solvent extraction system SISAK4 and with a thermochromatographic column where chemical selectivity is achieved by producing volatile species. Furthermore, approaches to achieve chemical separations in a gas-jet system itself are presented and the application of the various chemical procedures in nuclear spectroscopic studies is illustrated by a few examples.

2. Continuous chemical separation procedures

The gas-jet recoil-transport method3 has found widespread application as a rapid and efficient technique for transporting short-lived nuclides from the production site to detector systems or to separation facilities. In this method nuclear reaction products recoiling out of thin solid targets are stopped in a gas containing clusters and the thermalized atoms sticking to these clusters are transported along with the carrier gas out of a stopping chamber through a capillary to a low-background area. The sticking process is rather unselective with regard to the mass and atomic number of the reaction products and in most cases mass separation5) or chemical steps have to be added.

The development and application of the continuous chemical separation methods described below were performed with neutron-rich nuclei from thermal-neutron induced fission of 235U or 239Pu. Since gas-jets have mostly been used at accelerators, the techniques outlined in this paper are also applicable to products from charged particle induced reactions.

The fission products were produced by irradiation of 0.1-1 mg 238U or 239Pu targets in a thermal neutron flux of about 6x10^12 n/cm^2·s in one of the beam holes of the Mainz reactor. After thermalization in nitrogen containing clusters they were swept out through a 1 mm inner diameter polyethylene capillary.

2.1 Combination of a gas-jet with the solvent extraction system SISAK

The SISAK technique is based on continuous multistage solvent extraction procedures where the separation of the two phases is accomplished by specially designed centrifuges6). A set-up of four small centrifuges has been installed at the Mainz reactor and combined with a KCl/N2-jet7). This arrangement allows on-line nuclear spectroscopic studies on nuclides with half-lives down to about one second.

As an example Fig. 1 shows the separation of zirconium and niobium from a fission product mixture5) based on the solvent extraction with Alamine-336. The fission products carried by the gas-jet are dissolved in 1 M sulphuric acid in a static mixer. The gas-liquid mixture is then fed into a degassing unit, in which the carrier gas and more than 98% of the noble gases are separated from the aqueous solution and removed by suction. To enhance the degassing effect the temperature of the solution is kept at ~70°C. In the first mixer-
centrifugal separator unit (Cl) the aqueous phase is contacted with a 0.1 M solution of Alamine-336 in Shellsol-T (an aliphatic kerosene). The organic phase also contains n-dodecanol (5 %) to prevent formation of a third phase. Zirconium and niobium are extracted with high yield (\(\geq 80\%\)) into the organic phase, probably as negatively charged sulphate complexes. Technetium and a few other fission products (like iodine) are extracted to a small extent (\(< 5\%\)).

In the second mixer-centrifuge step (C2) zirconium and niobium are back-extracted almost quantitatively by means of 0.3 M nitric acid, while technetium and most of the other contaminants remain in the organic phase.

After the back-extraction step hydrogen peroxide is added to the aqueous solution for the complexation of niobium and to increase the acidity so that the solution entering the third mixer-centrifugal separator unit (C3) consists of \(\sim 3\) M nitric acid and \(\sim 1\) M hydrogen peroxide. In C3 approximately 95 % of the zirconium are extracted into 1 M solution of HDEHP (di-(2-ethylhexyl)-orthophosphoric acid) in Shellsol-T whereas niobium as peroxide complex remains in the aqueous phase. In the organic phase only zirconium nuclides and their daughter products can be observed, together with a very small amount of iodine; the aqueous phase still contains some zirconium activity which is removed in a further extraction step with HDEHP (C4). The average delay times from the target site to the detectors (maximum countrate at the detector) are 7 and 9 s for pure Zr- and Nb-fractions measured in the positions D(Zr) and D(Nb) of Fig. 1, respectively. The \(\gamma\)-ray spectra of the niobium fraction show no other \(\gamma\)-rays than those belonging to the nuclides \(99-100\text{Nb}\) and their decay products. The zirconium chemistry has been used for \(\gamma\gamma\) coincidence measurements on \(^{162}\text{Zr}\).

The chemical procedure for the separation of technetium from a \(^{239}\text{Pu}\) fission product mixture is shown in Fig. 2. Here, the fission products carried by the gas-jet are dissolved in a solution consisting of 0.1 M nitric acid and 0.1 M potassium bromate. The solution is heated to \(\sim 80\) °C to accelerate the oxidation of technetium to the pertechnetate ion and to achieve a better separation from the fission product noble gases. In the first mixer-centrifugal separator step (Cl) technetium is extracted into 0.05 M Alamine-336 in chloroform. Molybdenum and a small fraction of zirconium and niobium are co-extracted. In the next step (C2) technetium and traces of zirconium, niobium and molybdenum are back-extracted into 2 M nitric acid.

Table 1 Continuous chemical separation procedures with SISAK

<table>
<thead>
<tr>
<th>Separated element</th>
<th>Production mode</th>
<th>Transport system</th>
<th>Studied nuclides</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>(235\text{U}); thermal fission</td>
<td>Liquid ZnCl(_2)</td>
<td>(^{68}\text{Cu}, \text{70}\text{Cu})</td>
</tr>
<tr>
<td>As</td>
<td>(235\text{U}); thermal fission</td>
<td>Gas-jet</td>
<td>To be used for (^{85}\text{As})</td>
</tr>
<tr>
<td>Br</td>
<td>(235\text{U}); thermal fission</td>
<td>Gas-jet</td>
<td>(^{86-89}\text{Br})</td>
</tr>
<tr>
<td>Zr</td>
<td>(235\text{U}); thermal fission</td>
<td>Gas-jet</td>
<td>100 (\text{Zr})</td>
</tr>
<tr>
<td></td>
<td>Heavy-ion reaction</td>
<td>Gas-jet</td>
<td>To be used at GSI, Darmstadt</td>
</tr>
<tr>
<td>Nb</td>
<td>(235\text{U}); thermal fission</td>
<td>Gas-jet</td>
<td>Test</td>
</tr>
<tr>
<td></td>
<td>Heavy-ion reaction</td>
<td>Gas-jet</td>
<td>To be used at GSI, Darmstadt</td>
</tr>
<tr>
<td>Tc</td>
<td>(235\text{Pu}); thermal fission</td>
<td>Gas-jet</td>
<td>106-108 (\text{Tc})</td>
</tr>
<tr>
<td>Ru</td>
<td>(235\text{Pu}); thermal fission</td>
<td>Gas-jet</td>
<td>To be used for (^{109-112}\text{Ru})</td>
</tr>
<tr>
<td>Pd</td>
<td>(235\text{U}); 14-MeV fission</td>
<td>Liquid</td>
<td>116 (\text{Pd})</td>
</tr>
<tr>
<td>I</td>
<td>(235\text{U}); thermal fission</td>
<td>Gas-jet</td>
<td>Test</td>
</tr>
<tr>
<td>La</td>
<td>(235\text{U}); thermal fission</td>
<td>Gas-jet</td>
<td>143-148 (\text{La})</td>
</tr>
<tr>
<td>Ce</td>
<td>(235\text{U}); thermal fission</td>
<td>Gas-jet</td>
<td>145-150 (\text{Ce})</td>
</tr>
<tr>
<td>Pr</td>
<td>(235\text{U}); thermal fission</td>
<td>Gas-jet</td>
<td>147-150 (\text{Pr})</td>
</tr>
</tbody>
</table>
(or in some cases 0.8 M nitric acid; see below). In the third stage (C3) zirconium and niobium contaminations are removed by extraction with 0.5 M HDEHP in chloroform. The outgoing aqueous phase contains only technetium nuclides, their daughter products and a small Mo-contamination (< 1%).

\[ \gamma \gamma (t) \]-coincidence investigations on \( ^{106-108} \text{Tc} \) were carried out by measuring directly the aqueous phase leaving C3. For \( \gamma \gamma \)-angular correlation measurements on \( ^{106} \text{Tc} \) the system was modified in such a way that the technetium activity was back-extracted in C3 into 0.8 M HNO\(_3\), and after C3 0.7 M sodium hydroxide was added. The resulting solution was pumped through an empty detector cell of the same dimension as in the case of \( ^{106} \text{Tc} \) through which the aqueous phase from C2 was pumped with a flow-rate of \( \sim 10 \text{ ml/s} \). The measurements on neutron-rich technetium nuclides resulted\(^9\)\(^{11}\) in detailed decay schemes of \( ^{106-108} \text{Tc} \).

So far we have developed 12 different separation procedures\(^6\)^{13} with the SISAK system which are summarized together with their applications in Table 1. For the separation of arsenic a gas-jet with chemical selectivity (HCl-jet; see below) and a new, faster degassing unit with a hold-up time of \( \sim 0.3 \text{ s} \) compared to \( \sim 2 \text{ s} \) obtained with the former degasser was applied. With this arrangement an one step separation is sufficient for the isolation of arsenic yielding in a total transport time of 2.9 s (maximum countrate), determined by multiscaling of the arsenic fraction and operating the reactor in the pulse mode.

2.2. Combination of a gas-jet with a thermochromatographic column

In the combination of a gas-jet with a thermochromatographic column chemical selectivity can be achieved by producing volatile species in reactions with reactive gases which are swept by a carrier gas or in the vacuum through a tube with a negative temperature gradient and are deposited at temperatures correlated to the adsorption enthalpies and entropies of the volatile species. Fission products were used as a model for complex mixtures of elements and chlorides, bromides and iodides were chosen as volatile species.

A nitrogen gas-jet containing potassium chloride clusters is used to transport the fission products from the target area to the thermochromatographic system\(^{13}\) shown in Fig. 3. The clusters are stopped in a quartz-wool plug located in a quartz column with an inner diameter of 4 mm which is filled with quartz powder. The plug is heated to \( \sim 950 \text{ °C} \).

\[ \text{Fig. 3 Set-up for the thermochromatographic separation of fission product halides.} \]

In order to destroy the clusters and to enable complete halogenation. Along the thermochromatographic column a negative temperature gradient of \( 18 \text{ °C/cm} \) is established. After the column the gas passes through a charcoal trap which collects very volatile species and through a NaOH trap in which the halogenating agents are caught. To increase the flow rate through the thermochromatographic set-up an oil pump is placed behind the NaOH trap. For halogenation of the fission products a mixture of the reactive gas with nitrogen is fed into the column through a by-pass. The element distribution along the thermochromatographic column was measured after removal of the column from the oven by \( \gamma \)-ray spectroscopy. With HCl, HBr and HI quite similar thermochromatograms were obtained. As an example Fig. 4 shows the fission product distribution with HCl in the carrier gas at a flow rate of 1.3 l/min and after an exposure time of 15 min. The alkaline earth elements are not volatilized under these conditions. The lanthanides are deposited at 750 °C and Rb and Cs are found at 680 °C. Molybdenum forms a rather broad zone with two peaks at 590 °C and 410 °C. Proceeding to the low temperature region,
particle size. In this trap, bromine, iodine and selenium activities are absorbed to 95% whereas fission products fixed on clusters pass through a small column (Trap 1) packed with quartz-wool to retain activities attached to clusters.

with about 90% efficiency, accompanied by krypton and xenon activities. After this trap the gas mixture enters the reaction chamber consisting of a quartz spiral which is heated to 860°C. At this temperature, the clusters are decomposed and volatile compounds of tellurium are formed. These compounds and the noble gases are transported through a capillary to a trap filled with charcoal. Tellurium is completely absorbed in this trap whereas the noble gases pass through. At the exit of this trap, a pump was placed to decrease transport time and to improve decontamination from noble gas activities. It should be mentioned that beyond 900°C the decomposition of ethylene becomes vigorous as indicated by the formation of soot.

The set-up for the continuous separation of selenium from fission products is similar to the one used for tellurium (Fig. 5) except that the charcoal trap preceding the reaction chamber is replaced by two paper filters. In this filter, 99% of the activities attached to clusters are retained whereas selenium, the halogens and the noble gases pass through. Selenium and the halogens form volatile species in the reaction chamber but due to differences in the formation of the species and in the transport behavior, selenium and the halogens can be separated from each other. The decay time between production of Te and Se at the target and their collection in the final absorption trap was determined to be 6 s for 50% of the saturation activity.

Both on-line gas phase procedures have been applied for investigations on the decay properties of the neutron-rich nuclides $^85-88$Se and $^{135-137}$Te by γ-ray singles and coincidence measurements.

Highly volatile chlorides of germanium, arsenic and the halogens are formed from fission fragments recoiling into nitrogen containing hydrochloric acid as the reactive component and can be separated from each other on selective adsorbents. Fig. 6 shows the arrangement for the continuous separation of germanium from fission products. The reactive gas, a 1:20 mixture of hydrochloric acid and nitrogen and the volatilized fission products pass through a quartz spiral (Trap 2) which is coated at its inside with a silver layer and heated to about 800°C. In this spiral the halogens are transformed to nonvolatile species and adsorbed at the silver layer, whereas germanium, arsenic and the noble gases pass through. The following column (Trap 3) is filled with polystyrene beads saturated with HDEHP retaining the volatile arsenic compound almost quantitatively. The placement of a detector system close to the absorption position allows to measure short-lived arsenic activity on-line. Germanium chloride, passing this column, is collected in a charcoal trap (Trap 4) and its isotopes can be studied with a detector system placed there, as shown in Fig. 6. The noble gases are pumped off. The calculated transport time from target to detector is about 3 s and a transport yield of < 30% results for carrier-free germanium. The method described has been used for decay studies on the neutron-rich germanium isotopes $^{26.8}$Ge, $^{7.8}$Ge and $^{4.5}$Ge.

3. Conclusions

The combination of gas-jet recoil-transport systems with various chemical steps enables continuous separations of single elements from complex reaction product mixtures within a few seconds and, hence, offers an important approach for studies of nuclei far from the region of $\beta$-stability.
The continuous solvent extraction with the centrifuge system SISAK is applicable for the isolation of any element which can be distributed between two immiscible liquid phases. The gas-jet can be combined with thermochromatographic columns in a very simple way opening many possibilities for on-line studies on short-lived nuclides. Chemical reactions in a gas-jet system with reactive additives can be utilized for very fast on-line procedures for the isolation of certain elements.

The continuous performance is of importance in all measurements with low efficiencies such as delayed-neutron spectroscopy, yy-coincidence, high energy yy-ray and yy-angular correlation spectroscopy which require long-time operation in order to collect data of sufficient statistical quality. With regard to the time scale all the continuous procedures presented in this paper work in the second range. The future trends may be mainly directed towards the development of ultrafast chemical separations which should allow investigations on nuclides down to half-lives of milliseconds. Here the most promising way seems to be direct chemical reactions in a gas-jet recoil-transport system.

References