

FAST AQUEOUS CHEMISTRY ON-LINE WITH CYCLOTRON-PRODUCED ACTIVITIES USING A HELIUM-JET RECOIL-TRANSPORT SYSTEM

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A relatively simple system is described that can be used to perform fast on-line chemical separations (≤ 1 s) on activities transported to low background areas in the relatively short times provided by a helium-jet recoil-transport system. The

helium-jet recoil-transport system is run with its low-pressure end at atmospheric pressure, thereby eliminating the need for vacuum pumps and their associated apparatus.

1. Introduction

Details of the construction and operation of the Helium-Jet Recoil-Transport (HeJRT) system used in this work are given elsewhere^{1,2)} and numerous references to similar systems also exist³⁻⁷⁾. Accordingly, we mention only the specific parameters used and the modifications made to the HeJRT system that allowed the performance of fast on-line aqueous chemistry with it. Our HeJRT system presently employs a 14-m long, 0.0014-m i.d. polyethylene capillary between the target assembly and the chemistry apparatus. A small amount of benzene vapor (≈ 20 ppm) is added to the helium supply to generate the large cluster "molecules" which aid in the transport of activities through the system^{1,3,7)}. The target assembly volume was filled with helium and maintained at a pressure gradient of ≈ 2 atm across the system.

The initial hope that "wet" chemistry could be performed on-line with the HeJRT system arose from the observation that the efficiency of the HeJRT system when depositing activities on paper tape did not start to fall off until the pressure in the detector chamber (box where activities transported through the system are normally deposited on some collecting surface and counted) was raised to above 20-30 torr¹⁾. This was important because the vapor pressure of water at 20°C is 17.5 torr. Accordingly, if it were possible to introduce the activities transported through the system into an aqueous solution, it would be possible to

consider aqueous chemistry without having the solutions boiling off. (Actually, we have since discovered that the HeJRT system can be operated successfully with its low-pressure end at atmospheric pressure, making chemical procedures even simpler.)

We have been able to carry out a number of different chemical separations more or less successfully. Some have been semi-on-line, others completely on-line and fast. The most successful to date is the separation of 33-s ⁶³Ga from 38-min ⁶³Zn and 24-min ⁶⁰Cu, which is described in some detail in section 2. [A preliminary version of this separation was presented at the New York APS Meeting in January 1973⁸⁾]. It now appears that the numbers and types of different fast chemical separations that can be performed in conjunction with a HeJRT system should be essentially unlimited, making it an even more powerful tool than heretofore realized.

2. Experimental procedures

The first successful chemistry performed with the HeJRT system followed the discovery that not only is it possible to trap activities flowing up the capillary in aqueous solution merely by bubbling the helium flow from the capillary through the solution, but also that the yields remained essentially as good even if the low-pressure end of the capillary and the aqueous solution were at atmospheric pressure. In a series of experiments comparing the amounts of activity trapped in solution under various pressures to that collected on paper tape under ≈ 1 torr pressure, it was observed that between 1/2 and 2/3 of the activity could be collected in the aqueous solutions. The amount of activity trapped was largely independent of the pressure over the

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solution (the pressure gradient across the total system was held constant at ≈ 2 atm). The amount of activity trapped was also found to be independent of the acid concentration of the trapping solution (for most common acids) – this is important if chemistry is to be performed. We felt that much of the activity lost might have been retained by the solution had we generated smaller bubbles (with correspondingly higher surface-to-volume ratios), but when one is dealing with short-lived activities it is necessary to flow the helium through the solution as fast as possible.

If one accepts the role of the "molecular" clusters to be that of providing for the efficient transport of activities through the system because of these activ-

ities' attaching themselves to the clusters, then it does not necessarily follow that if one can trap activities in a solution it will be possible to perform conventional chemistry with these activities. If the thermalized recoils become a part of the cluster molecules at some point during the transport process, then it should not be possible to perform chemistry characteristic of the recoil activity unless it can be successfully freed from the cluster molecules. The reason for this is simply that the recoil activity is present only as a very small component (less than about a part per million) in the recoil-cluster combination. Thus, if the recoils remain attached to the clusters after they are trapped in a solution, one would expect the combination to follow

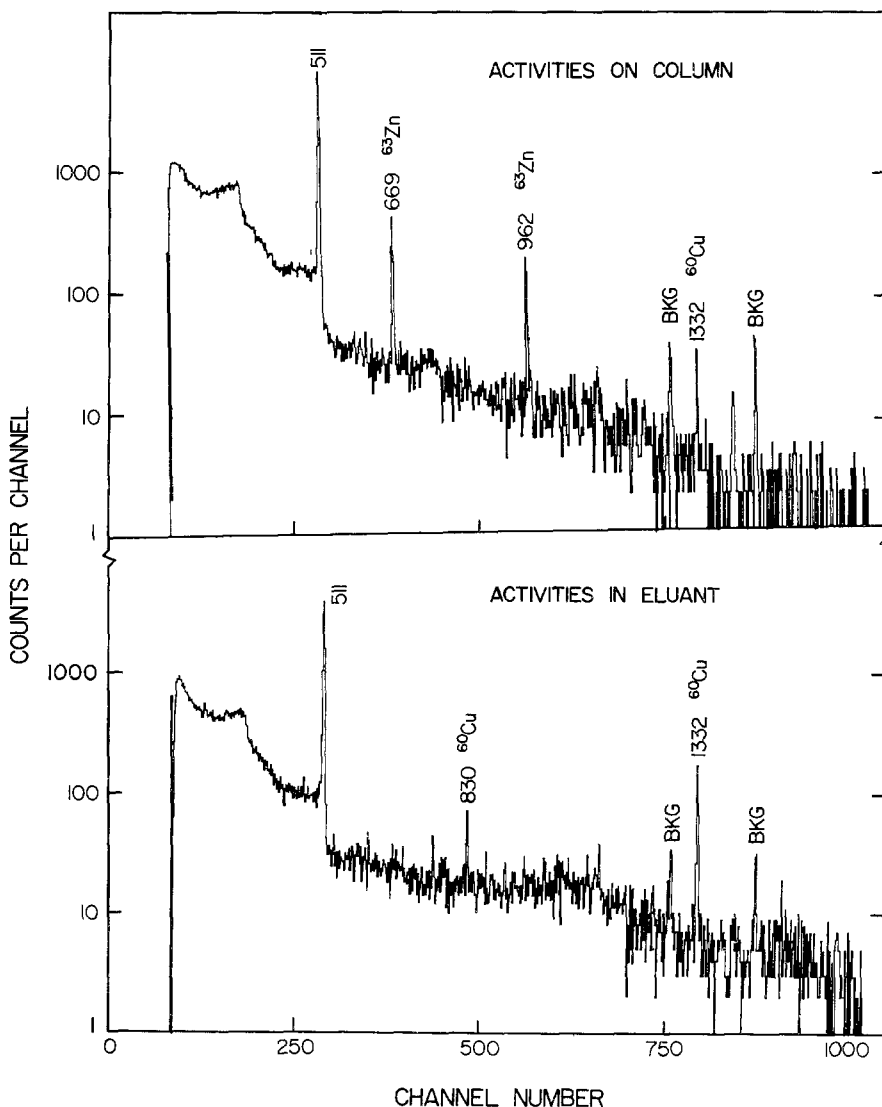


Fig. 1. Zn and Cu γ -ray spectra recorded in the first successful attempt at performing aqueous chemistry with the HeJRT system.

chemistry characteristic of the cluster and not the recoil. It is observed that cluster molecule deposits are soluble in water; however, it still does not necessarily follow that it will be possible to perform chemistry successfully with the recoils. If the recoil be deeply imbedded in the cluster molecule and if the individual cluster molecules retain much at all of their integrity upon dissolving, then the recoil would not necessarily be expected to be freed from the cluster in the dissolution process.

2.1. BATCH CHEMISTRY

Surprisingly, our first attempt at performing chemistry with activities transported by the HeJRT system and trapped in aqueous solution at atmospheric

pressure was successful. This was the separation of Cu and Zn activities using ion-exchange techniques. A natural Zn target was bombarded with 30-MeV protons from the Michigan State University Sector-Focused Cyclotron. The principal activities generated were (33-s) ^{63}Ga and (24-min) ^{60}Cu from the (p, 2n) and (p, α n) reactions on ^{64}Zn . The activities were transported through the HeJRT system and were trapped in a 2N HCl solution by simply letting the helium flow from the capillary bubble through a small beaker of the acid under atmospheric pressure. Activities were collected for about 25 min. During this 25-min collecting time and a short additional time before the activities were loaded on the ion-exchange column, essentially all the ^{63}Ga had decayed to (38-min) ^{63}Zn . The column was loaded with Dowex 1 \times 8 anion-exchange resin in the chloride form. The column was subsequently eluted with an additional small amount of 2N HCl, then the column and the eluant were each counted for about 10 min using a 4.6% efficient Ge(Li) detector. The spectra recorded are shown in fig. 1. It appears that the separation was rather clean in that there is no evidence of either Zn line appearing in the eluted sample and only a small amount of Cu was not completely eluted from the column as evidenced by the weak appearance of the 1333-keV line in the spectrum from the column.

The observation that straightforward chemistry characteristic of the recoil activity is successful with activities transported by the HeJRT system suggests that somehow the recoil has been freed from the recoil-cluster combination. A discussion of possible mechanisms for freeing the recoil would not be profitable at this time, as more and detailed experiments would have to be performed to study such mechanisms. Also unknown at this point was the time required for freeing the recoils from the clusters. This time was obviously less than the 5–10 min that elapsed between the end of collecting the activities in the experiments described above and the passage of these activities through the ion-exchange column. If it were much longer than this, it would not have been possible to have so clean a chemical separation. Zn activities still trapped in the clusters would have passed through the column, resulting in Zn lines being present in the spectra from the eluted samples.

2.2. ON-LINE, CONTINUOUS CHEMISTRY

The next attempt at performing chemistry on activities transported by the HeJRT system was an attempt at on-line chemistry. This was a separation of Ga from both Cu and Zn activities using ion-exchange tech-

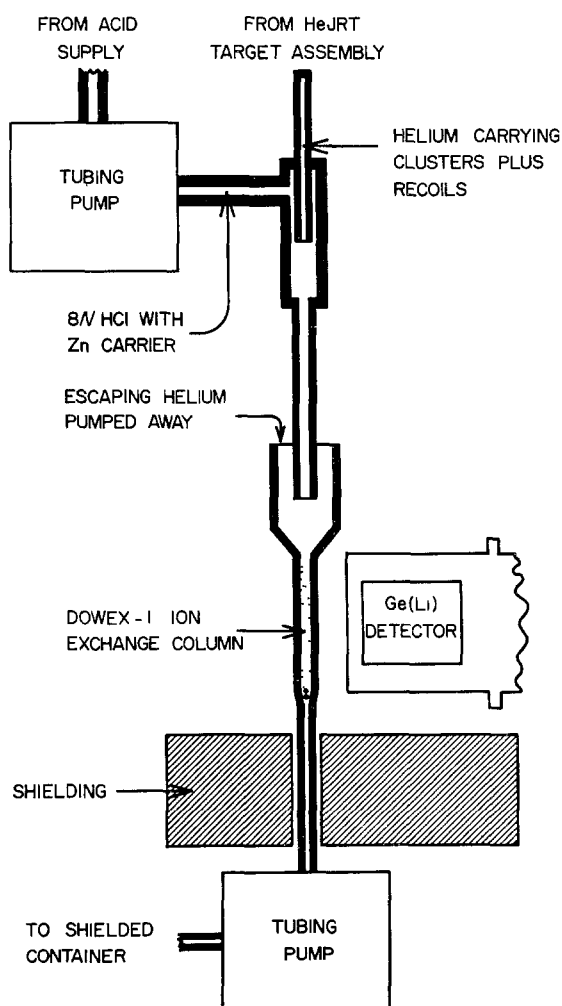
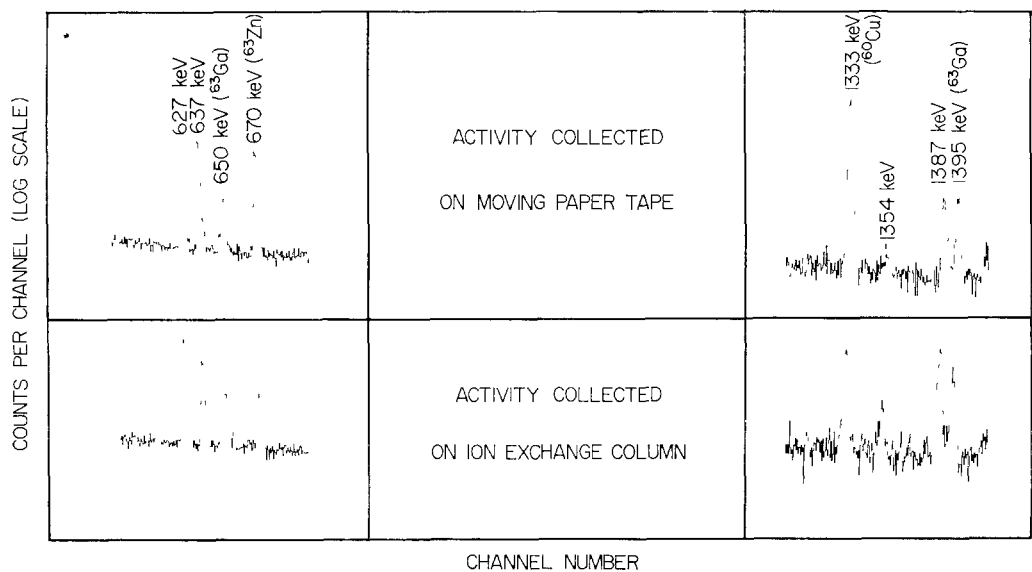


Fig. 2. Sketch of the experimental apparatus used for on-line separation of Ga from Zn and Cu activities after these had been transported to a low-background area with a HeJRT system.

niques. As in the previous attempt, a natural Zn target was bombarded with 30-MeV protons, producing primarily the same (33-s) ^{63}Ga and (24-min) ^{60}Cu activities. Also present was some ^{63}Zn from the partial decay of ^{63}Ga and from a (p, pn) reaction on ^{64}Zn . However, time was not allowed in this experiment for the ^{63}Ga to decay appreciably to ^{63}Zn . The flow from the capillary of the HeJRT target assembly entered directly into the chemical apparatus (cf. fig. 2) and was mixed with a flow of 8N HCl (containing carriers) pumped from a container of acid. The mixing took place in a small chamber and was quite turbulent because of the large volume of He flowing from the target assembly (≈ 40 std cm^3/s). The mixture of He and acid moved rapidly to the top of an ion-exchange column, again because of the large volume of He flowing. Here the acid solution was allowed to enter the column while the escaping He, presumably still carrying some activities, was pumped away. The ion-exchange column was loaded as before with Dowex 1×8 anion-exchange resin in the chloride form; a rather large mesh (50–100) was used to decrease the hold-up time of the column. The acid solution was drawn through the column and pumped to a shielded container, and a 4.6% efficient Ge(Li) detector was

used to record the γ -ray spectra of the activities on the column.

To serve as a comparison, an experiment was performed where the same activities were collected on moving paper tape under vacuum. The tape speed was such that the activities on the tape spent ≈ 1 min before the Ge(Li) detector. Two short sections of the spectra recorded in this experiment are shown in fig. 3, along with a comparison of the results. Further comparisons with a previous set of experiments by Giesler in this laboratory⁹⁾ using a pneumatic target system ("rabbit") are also shown in this figure. The relative intensity of the ^{60}Cu to the ^{63}Ga peaks in the chemistry experiment are down by a factor of six over those in Giesler's experiments and by a factor of five over those in the paper-tape experiments. The ^{63}Zn relative to the ^{63}Ga peaks in the chemistry experiment are down by a factor of more than two over those in Giesler's experiments. Further, the data acquisition rate was up by a factor of about two for the chemistry experiment over Giesler's experiments, using approximately the same bombarding techniques. The possibility that the improvement in the ^{63}Ga to ^{60}Cu and ^{63}Zn ratios was just a half-life effect is eliminated by the presence of (2.6-min) ^{64}Ga and (15-min) ^{65}Ga



Ratio $^{63}\text{Ga}(650)/^{63}\text{Zn}(670)$

Rabbit run	0.42
Collecting on tape	0.62
Collecting on column	0.98

Ratio $^{63}\text{Ga}(1395)/^{60}\text{Cu}(1333)$

Rabbit run	0.11
Collecting on tape	0.15
Collecting on column	0.72

Fig. 3. Portions of the γ -ray spectra recorded using the set-up of fig. 2 for performing fast on-line aqueous chemistry and comparisons with results from previous experiments.

peaks at 1387 and 1354 keV, respectively, in the chemistry experiment spectrum.

This experiment provides an improved upper limit for the time necessary to free recoils from the molecular clusters in aqueous solutions. The time elapsing between the mixing of the He and acid flow and then the acid solution's leaving the ion-exchange column was less than 1 s. Accordingly, the upper limit on the time necessary to separate recoil and cluster should be set at ≈ 1 s in this case. A check of the eluant from the column should have been made to see if any Ga activities were present; if they were not, the upper time limit of 1 s would be more definite. However, from the data collection rate observed it is certain that at least a large fraction of the recoils had been separated from the clusters in this 1-s elapsed time.

We are currently performing a series of experiments that will attempt to set a definite upper limit on the time necessary to separate recoils from clusters and also to demonstrate further the usefulness of this technique by performing separations on successively shorter-lived activities (and, incidentally, to determine more precisely the transit times through the capillaries in HeJRT systems). Some preliminary results have been obtained showing that it is possible to separate (2.1-s) ^{24}Al from (0.39-s) ^{20}Na . There is some hope that this series will culminate in the separation of (182-ms) ^{40}Sc from other reaction products

3. Conclusions

It is clear that much of the detail of the mechanisms allowing conventional aqueous chemistry to be performed on activities transported by the HeJRT system is not presently understood, indeed much of the mechanism of transport itself is not known. The points made in this paper, however, are that it is quite possible to perform straightforward aqueous chemistry with the HeJRT system, that the chemistry can be very fast (≤ 1 s), and that only a minimum of equipment is necessary. The fact that chemistry can be performed with the HeJRT system operated in the foregoing

manner has many implications associated with the mechanism through which a HeJRT system operates; however, these are beyond the scope of this paper.

It should be pointed out further that the number of chemical separations that should become practicable with a HeJRT system must be legion – many very short-lived activities that have heretofore not been available for chemical separation should be amenable to separations in conjunction with a HeJRT system. Also, there should be additional applications, beyond just rapid nuclear chemical separations. One of these could be to supply chemically active isotopes, in times ≤ 1 s, that are carrier and parent free for use in biological, medical, or other chemical studies.

Subsequent to the presentation of our initial on-line chemistry results^{2,8}), we received a report of an approach involving a fast batch chemical process¹⁰) similar in principle to our first separation at atmospheric pressure, as described in the previous section.

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