

## The Separation of Small Amounts of Inorganic Cations by Chromatographic Methods. III. Spallation of Copper with 60 MeV Protons

GÖRAN CARLESON

*The Gustaf Werner Institute for Nuclear Chemistry, University of Uppsala, Uppsala, Sweden*

Chromatographic paper strip technique is tested to separate the spallation products of copper. Complete separation of the whole group is obtained in about 3–4 hours, and a special monitor is hence not wanted. The yields of isotopes with half-lives above 30 minutes can be determined.

Bombardment of Cu by charged particles with energies ranging from 1–400 MeV have been carried out and the yields of radioactive products, formed during the high energy process, reported<sup>1-4</sup>. The present investigation was performed to study the yield distribution in an intermediate range, 60 MeV, and also to test the utility of chromatographic paper strip technique<sup>5-6</sup> in spallation studies.

### EXPERIMENTAL

a) *Irradiations* with 60 MeV protons were carried out in the circulating beam of the Uppsala synchro-cyclotron during 30–60 minutes with 0.1 mm thick electrolytic Cu-foils, dimensioned 2 × 16 mm, as targets.

b) *Separation procedure.* The Cu-foil was dissolved in hot HCl + H<sub>2</sub>O<sub>2</sub>, the copper precipitated as sulfide by H<sub>2</sub>S and separated from the solution by centrifuging. All the spallation products, except almost all Cu, remained in solution, which was gently evaporated to a small volume on a steam bath, a slow warm air-stream passing through the solution. An exact volume was applied to two paper strips by means of a thoroughly calibrated micro-pipet. After 15 minutes equilibration in the chromatography chambers, the complete separation of the different cation species was attained by eluting one strip with methyl-*n*-propyl ketone + 15 % 8 M HCl and the other with the same ketone + 15 % 10 M HCl (see Figs. 4–5 in part II of this work), and their exact positions on the strips registered by special counting equipment<sup>6</sup>. Each ion-species, Mn and Ni from the second solvent mixture, Co, Zn, Fe, and Cu-contaminations from the first, was completely cut out from the strips, gently ashed into a small Pt-dish, the same as was used in the later radiometric analysis.

The Cu-precipitate was dissolved in concentrated HNO<sub>3</sub>, and an exact volume pipetted into a Pt-dish. The total volume of the Cu-solution as well as the solution, containing the other ions, was determined.

Before the first spallation experiment, an investigation was made into the possible losses of both Cu and "other" isotopes during precipitation, evaporation and ashing, using both inactive and active isotope mixtures. The Cu-fraction was found to be entirely uncontaminated by the "other" ions. This was also verified in each spallation experiment as well as the Cu-losses, the latter obtained by weighing the foil before bombardment and by quantitative Cu-determination after the transfer of the aliquot to the Pt-dish. The losses of "other" isotopes were found to be  $(7 \pm 2)$  %, and they principally occur during evaporation. The losses in the ashing procedure, though found to be negligible ( $<1$  %), were always checked.

c) *Counting technique.* The isotopes were identified by half-life determinations and absorption measurements by means of a sample changer arrangement and an end-window GM-counter (Philips 8314), mounted in a lead castle with good geometry and negligible housescattering. Corrections were made for background, coincidence, backscattering, air and window absorption, decay during bombardment and counting efficiency of the rays.

Yields are given relative to  $\text{Cu}^{64}$ , which is arbitrarily assigned a yield 1.00.

#### IDENTIFIED RADIOACTIVE NUCLIDES

a) *Zn-fraction.*  $\text{Zn}^{62}$  and  $\text{Zn}^{65}$  were identified.  $\text{Zn}^{62}$  was counted in equilibrium with its daughter element  $\text{Cu}^{62}$  and is assumed to decay 10 % by  $\beta$ -emission and 90 % by K-capture.  $\text{Zn}^{65}$  was assumed to decay 46 % by  $\gamma$ -emission and was counted through sufficient Al-absorber to cut out completely the  $\beta$ - and X-rays, and the counting efficiency of the 1.1 MeV  $\gamma$ -ray was assumed to be 1.7 %. The half-life of  $\text{Zn}^{63}$  was too short to be counted by the technique, employed.

b) *Cu-fraction.* Identified activities were those of  $\text{Cu}^{60}$ ,  $\text{Cu}^{61}$ ,  $\text{Cu}^{62}$  and  $\text{Cu}^{64}$  with counting efficiencies, estimated to be 101, 67.8, 100.5 and 59 %.

c) *Ni-fraction.* The only observed activity was that of  $\text{Ni}^{57}$ , which was assumed to decay 50 % by  $\beta$ -emission with a total counting efficiency of 55 %.

d) *Co-fraction.* The radionuclides  $\text{Co}^{56}$ ,  $\text{Co}^{57}$ ,  $\text{Co}^{58}$ ,  $\text{Co}^{60}$  and  $\text{Co}^{61}$  have been identified, and their counting efficiencies were assumed to be, respectively, 98, 100, 17.6, 103 and 100 %. Even the 9.2 hour  $\text{Co}^{58}$ -isomer was identified. The counting efficiency in the GM-counter of a 0.025 MeV  $\gamma$ -ray is 2.7 %, which was assumed to be the efficiency for the isotope. The yield of the short-lived  $\text{Co}^{62}$  cannot be determined with the separation technique, employed.

e) *Fe-fraction.* The activities of  $\text{Fe}^{55}$ ,  $\text{Fe}^{59}$  and  $\text{Fe}^{60}$  were identified.  $\text{Fe}^{55}$  is assumed to decay 100 % by K-capture with a counting efficiency of 3.5 % and  $\text{Fe}^{59}$  100 % by  $\beta$ -decay.

In the iron decay curve a new activity was found, presumably due to the earlier reported, though uncertain,  $\text{Fe}^{60}$ -isotope, identified in fission studies at Berkeley<sup>7</sup>. In three bombardments its half-life was found to be 8.3, 8.1 and 8.1 hours. The  $\beta$ -energy was calculated to be  $1.6 \pm 0.2$  MeV by absorption measurements, which also indicated that the counting efficiency of the isotope + daughter is only about  $(8 \pm 5)$  %. The mass number is, however, not established, but the yield, found, supports the assumption that the isotope is  $\text{Fe}^{60}$ , and the  $\beta$ -energy, found, is in agreement with the energy of the daughter element  $\text{Co}^{60}$ . The  $\beta$ -energy of the new isotope is hence unknown. The possibility that the isotope is  $\text{Fe}^{52}$  can be eliminated, as the threshold energy with deuterons for  $\text{Cu} \rightarrow \text{Fe}^{52}$  has been reported to be 85 MeV<sup>3</sup>, and the threshold energy with protons can hardly be more than 10 MeV less. Neither the counting efficiency found, nor the  $\beta$ -energy corresponds to  $\text{Fe}^{52}$ .

f) *Mn-fraction*. The characteristic activity of  $Mn^{56}$  was identified as well as a very weak  $Mn^{54}$ -activity, but no  $Mn^{52}$ -activity was found. Counting efficiency of  $Mn^{56}$  was assumed to be 102 % and of  $Mn^{54}$  6 %.

g) Neither Cr- nor V- activity was observed.

## EXPERIMENTAL RESULTS

Table 1 shows the partly corrected yields in 4 bombardments together with their weighted means, and Table 2 the finally corrected yields.

Table 1. Experimental yields from Cu, irradiated with 60 MeV protons; yields are relative to  $Cu^{64}$ .

Iso- tope	Experimental number								Weighted mean	
	I		II		III		IV			
	$\tau_{\frac{1}{2}}$	yield	$\tau_{\frac{1}{2}}$	yield	$\tau_{\frac{1}{2}}$	yield	$\tau_{\frac{1}{2}}$	yield		
$Mn^{54}$									0.00023	0.00023
$Mn^{56}$	2.80 h	0.00362	2.59 h	0.00360	2.70 h	0.00367	2.75 h	0.00158	0.0036	0.0036
$Fe^{59}$				0.0172	46.0 d	0.0055	45.5 d	0.0047	0.0055	0.0055
$Fe^{60}$	8.3 h	0.000102			8.10 h	0.000188	8.1 h	0.000169	0.00075	0.00075
$Co^{56}$						0.0088			0.009	0.009
$Co^{57}$		0.068		0.050		0.073		0.051	0.060	0.060
$Co^{58}$	9.4 h	0.004			9.15 t	0.00382	9.3 h	0.0035	0.0037	0.0037
$Co^{60}$		0.188		0.147		0.188		0.157	0.17	0.17
$Co^{61}$	1.80 h	0.055	1.83 h	0.0370	1.75 h	0.0565	1.74 h	0.0473	0.052	0.052
$Ni^{57}$	35.9 h	0.0276	36.0 h	0.0322	35.9 h	0.0323	35.2 h	0.0176	0.032	0.032
$Cu^{60}$					23.2 m	0.91	23.8 m	0.83	0.87	0.87
$Cu^{61}$	3.3 h	2.88	3.4 h	2.52	3.43 h	2.45	3.35 h	2.61	2.6	2.6
$Cu^{62}$							9.6 m	2.06	2.06	2.06
$Cu^{64}$	12.8 h	1	12.8 h	1	12.8 h	1	12.7 h	1	1	1
$Zn^{62}$			9.15 h	0.42	9.18 h	0.50	9.26 h	0.31	0.40	0.40
$Zn^{65}$						0.0059		0.0030	0.0046	0.0046

Table 2. Experimental yields, relative to  $Cu^{64}$  from Cu, irradiated with 60 MeV protons.  $\times$  stable isotopes.

	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66
$Zn_{30}$											0.21		$\times$	0.14	$\times$
$Cu_{29}$									0.71	2.20	3.10	$\times$	1	$\times$	
$Ni_{28}$						$3.15 \cdot 10^{-3}$	$\times$		$\times$	$\times$	$\times$		$\times$		
$Co_{27}$				0	$5 \cdot 10^{-3}$	$6.8 \cdot 10^{-2}$	0.58	$\times$	0.137	$2.8 \cdot 10^{-2}$					
$Fe_{26}$	0		$\times$		$\times$	$\times$	$\times$	$3.90 \cdot 10^{-3}$	$1.18 \cdot 10^{-3}$						
$Mn_{25}$	0		$2.66 \cdot 10^{-3}$	$\times$	$1.99 \cdot 10^{-3}$										
$Cr_{24}$	$\times$	$\times$	$\times$												

\* uncertain.

Mass number  $\longrightarrow$

## DISCUSSION

The greatest advantage of using the chromatographic technique is that particularly pure samples of all spallation products can simultaneously be obtained, as indicated by the agreement of half-life determinations with earlier published data. Exact calculations of the yields are hence favoured. Unfortunately the conventional radiometric weighing procedure cannot be used, the amounts being too small to obtain reliable weights without a sensitive micro-balance, and instead less accurate volumetric measurements must be made. The good reproducibility, attained in almost all bombardments as shown in Table 1, indicates, however, that the chromatographic procedure is well applicable to the study of spallation products, and on account of the small amount of work necessary, and the many yield determinations, simultaneously made in one bombardment, the method is in most aspects superior to the conventional technique.

The proton energy in bombardment IV in Table 1 was a little less than 60 MeV, and this is also shown by the yields of Mn<sup>56</sup> and Ni<sup>57</sup>, which were found to be considerably smaller than in the other bombardments, and depends on a steep fall of the excitation functions of Mn<sup>56</sup> and Ni<sup>57</sup> immediately below 60 MeV. Such a fall has earlier been found with deuterons just around 60 MeV<sup>3</sup>.

*Acknowledgement.* The author wishes to express his gratitude to Professor The Svedberg for his very kind interest throughout this work and to Professor S. Claesson for valuable advice and discussions. He is also very much indebted to Fillic. G. Rudstam for his revision of the manuscript. The investigation was financially supported by *The Swedish Atomic Energy Commission*, which is gratefully acknowledged as well as the permission to publish the results.

## REFERENCES

1. Hintz, N. M. and Ramsey, N. F. *Phys. Rev.* **88** (1952) 19.
2. Livingstone, R. S. and Wright, B. T. *Phys. Rev.* **58** (1940) 656.
3. Bartell, F. O., Helmholtz, A. C., Softky, S. O. and Stewart, D. B. *Phys. Rev.* **80** (1950) 1006.
4. Batzel, R. E., Miller, D. R. and Seaborg, G. T. *Phys. Rev.* **84** (1951) 671.
5. Part I of this work. *Acta Chem. Scand.* **8** (1954) 1673.
6. Part II of this work. » » » **8** (1954) 1693.
7. Folger, R. L., Stevenson, P. C. and Seaborg, G. T. UCRL-1195.

Received June 15, 1954.