CONF-870430--14

Analysis of Long-Lived Isotopes by Liquid Scintillation Spectrometry*

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International Conference on Methods and Applications
of Radioanalytical Chemistry
Kona, Hawaii
April 5-10, 1987

*Work supported by the U. S. Department of Energy.

Analysis of Long-Lived Isotopes by Liquid Scintillation Spectrometry

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Abstract

Neutron production cross sections are reported for reactions leading to long-lived isotopes in fusion reactor materials. Pure elements and separated isotopes were irradiated with 14.6-14.8 MeV neutron fluences up to 10^{18}n/cm^2. Undesired activities were chemically separated and the long-lived activities were measured using both liquid scintillation and x-ray spectrometry. Results are presented for the reactions ^{56}Fe(n,2n)^{55}Fe (2.73 y), ^{64}Ni(n,2n)^{63}Ni (100 y), ^{63}Cu(n,p)^{63}Ni, and ^{60}Ni(n,2n)^{59}Ni (76,000 y).

Introduction

Long-lived isotopes in fusion reactor materials are of interest due to waste disposal restrictions. However, production data are scarce for these isotopes since direct measurements must contend with very weak activities in the presence of numerous, stronger activities from competing reactions and impurities. Previously we have reported data for the ^{27}Al(n,2n)^{26}Al (720,000 y)[1], ^{94}Mo(n,p)^{94}Nb (20,300 y), and ^{92}Mo(n,x)^{91m}Nb (700 y) reactions[2]. In this study, we have measured the production of radioisotopes which decay by electron capture or beta decay. These radioisotopes can be measured by liquid scintillation counting; however, the analysis is complicated by the presence of unwanted activities. We have used radiochemistry to separate some of these undesired activities and have analyzed the liquid scintillation energy spectra to resolve the specific activity of interest. Gamma and x-ray spectrometry were used to confirm the separations and identifications of radioisotopes.

Sample Preparation and Irradiation

The samples consisted of the pure elements Fe and Cu, and separated isotopes of ^{56}Fe, ^{60}Ni, and ^{64}Ni, obtained from Oak Ridge National Laboratory, Oak Ridge, TN.

The separated isotopes of Fe, and Ni, were powdered metals packed in thin aluminum tubing measuring 1.5-2.0 mm o.d. by 10-14 mm long. The natural Fe and Cu metal samples were pressed into discs measuring 3 mm o.d. by 1 mm thickness. All samples were packaged for irradiation with thin (0.02 mm) Fe and Nb dosimetry foils in thin (0.01 mm) Al wrapping.

The activities were produced during several separate 14 MeV neutron irradiations to high fluences (10^{17}-10^{18} n/cm^2) at the Rotating Target Neutron Source II at Lawrence Livermore National Laboratory, Livermore, CA. At forward angles, neutrons are produced in the energy range from 14.5-14.8 MeV with an energy spread of several hundred keV. Details of the neutron energy spectra have been discussed in previous publications.[2] Iron and niobium dosimetry foils were included with each sample to determine the actual neutron fluence at each sample location using the well-known ^{54}Fe(n,p)^{54}Mn and ^{93}Nb(n,2n)^{92m}Nb reactions. A neutron fluence map was then produced for each irradiation; more detailed results have been published previously.[3]

Chemical Procedures

The analysis of each sample begins with gamma spectroscopy to determine the presence of other stronger activities. Based on these results, radiochemical separations are planned in order to separate as many undesired activities as possible. Gamma spectroscopy is used to determine the degree of separation and to establish the residual activities which were not removed. The purified sample is then counted by liquid scintillation spectroscopy. The scintillation energy spectrum is recorded and analyzed to separate the desired activity from the residual contaminants. Standards are used where possible to determine the desired spectral response and to establish the instrumental efficiency. This technique has been successful in resolving many of the desired long-lived activities. Details of the chemical and spectral separations are given below for each isotope.

Preparation of Standard Solutions

Standard solutions of ^{55}Fe and ^{63}Ni were obtained from Amersham International. Liquid scintillation samples were prepared for each reaction product depending on the expected count rate and dissolution required. Natural Fe, Ni, or Cu was added to the solutions to match the weight of the irradiated material. Hence, the quenching factors were identical for the standard and unknown activities, as confirmed by comparison of the energy spectra. In the case of ^{59}Ni, the spectrum was assumed to be similar to that of ^{55}Fe since the x-rays and conversion electrons only differ in energy by about 1 keV. The ^{55}Fe standard activity was 12.51μCi/g $\pm$4.3% and the ^{63}Ni standard was 13.02μCi/g $\pm$2.5%. The ^{59}Ni x-rays were counted using a thin, intrinsic Ge detector which was calibrated using ^{54}Mn, ^{55}Fe, ^{137}Cs, and ^{241}Am standards.

^{55}Fe Measurements

^{55}Fe has a halflife of 2.73$\pm$.03 y and decays by electron capture producing Auger electrons and x-rays near 6 keV [4]. ^{55}Fe was produced by the $^{56}Fe(n,2n)$ reaction from natural Fe and isotopically separated ^{56}Fe(99.87%). The principal unwanted activities in the samples were ^{51}Cr, ^{54}Mn, ^{57}Co, and ^{58}Co. The first two were produced by reactions on ^{54}Fe, principally in the natural Fe target whereas the Co activities were observed from Co and Ni impurities in the ^{56}Fe samples.

After sample dissolution with 8 N HCl, an aliquot was taken to dryness. In order to ensure that the iron was in the ferric (3^+) state, 8 N HNO_3 was added and the solution was again heated to dryness. After evaporation, 8 N HCl was added and the solution was again taken to dryness to destroy any remaining HNO_3. The final residue was then dissolved in 4 N HCl and placed on a preconditioned (4 N HCl) ion-exchange column. This column measured 10 cm high by 0.7 cm diameter and contained Bio-Rad AG 1x8 resin. Under this condition, the Fe^{+3} is adsorbed while the unwanted Co, Cr, and Mn nuclides are eluted.[5] The iron was then stripped from the column with 0.1 N HCl. Aliquots of this final solution were then added to a liquid scintillation cocktail

(Beckman HP) for counting. Small aliquots were also dried on Al plates for gamma counting to confirm that the undesired activities had been removed.

Figure 1 shows the liquid scintillation spectra for ^{55}Fe both from our samples and the standard solution. The data are given in Table I. As can be seen, our results for the ^{56}Fe(n,2n)^{55}Fe cross sections near 14.8 MeV have a standard deviation of only 2.6%.

^{63}Ni Measurements

^{63}Ni has a halflife of 100.1±2.1 y and decays by β^- emission with an end-point energy of 66 keV (average energy = 17 keV). ^{63}Ni was produced by the ^{64}Ni(n,2n) and ^{63}Cu(n,p) reactions. The ^{64}Ni was enriched to 93.57% and the copper had the natural abundance of 69.17% for ^{63}Cu. The ^{64}Ni samples contained undesirable activities of ^{54}Mn, ^{57}Co, ^{58}Co, and ^{60}Co, whereas the Cu samples contained mainly ^{60}Co.

All of these unwanted activities were easily removed by ion-exchange separations.[6] The procedure was similar to that for iron except that the nickel was initially dissolved in 8 N HNO_3, taken to dryness, then dissolved with 12 N HCl and added to a preconditioned (12 N HCl) AG 1x8 ion-exchange column. Under these conditions, the Co and Mn are adsorbed while the Ni is eluted. In the case of copper, the sample was dissolved in 8 N HNO_3, converted to 8 N HCl, and added to the anion exchange column. The Co and Cu were adsorbed on the column while the Ni was eluted.

In both cases, no residual activities were detected by gamma spectroscopy. Samples were prepared from the ion-exchange column wash and all of the unwanted activites could be accounted for within a few percent. Figure 2 shows the liquid scintillation spectra for each case, both before and after chemical separations, as well as the spectra from the standard solutions. As can be seen, the spectra from the separated materials closely match that of the standards. The neutron cross section data for each sample are listed in Table I. Again we note that the scatter in the data is only 1.5% for both the Ni and Cu samples.

^{59}Ni Measurements

^{59}Ni has a halflife of 7.5±1.3x10^4 y and decays by electron capture emitting about 6 keV Auger electrons and 7 keV x-rays [4]. ^{59}Ni was produced from the ^{60}Ni(n,2n) reaction using separated isotopes of ^{60}Ni (99.81%). The principal unwanted activities were ^{54}Mn, ^{57}Co, ^{58}Co, and ^{60}Co.

The chemical procedures were initially the same as for ^{63}Ni. Although the Co activities were readily separated by ion-exchange, it proved difficult to sufficiently remove the ^{54}Mn. Successive attempts with stronger acid solutions and longer columns eventually succeeded in removing about 99.7% of the ^{54}Mn. However, even at this level the residual activity was found to be comparable to that from ^{59}Ni. It should be noted that this was not a problem in the ^{63}Ni case since the initial level of ^{54}Mn was much lower and the specific activity of ^{63}Ni is many orders of magnitude larger than for ^{59}Ni. Furthermore, the spectrum may contain a contribution from ^{63}Ni. In spite of the low ^{64}Ni content (less than 0.02%), our present measurements of the (n,2n) reactions indicate that the ^{63}Ni activity could be comparable with that of ^{59}Ni. At best, the liquid scintillation data indicate that the ^{60}Ni(n,2n) cross section at 14.8 MeV is less than 200 mb.

Consequently, we decided to concentrate on counting the 7 keV x-rays from the decay of ^{59}Ni which have an intensity of 33.1±1.7% [4]. Samples were prepared from the purified Ni elutant by evaporating several milligrams of Ni onto an aluminum counting plate. Net corrections on the order of 10% were applied for self-absorption and scattering. In this case ^{63}Ni does not interfere since the β^- decay produces no Co x-rays. Data are listed in Table I. Uncertainites are larger for this reaction due to poorer counting statistics and the large (17%) uncertainty in the halflife.[4]

Comparison With Previous Data

All of the measured neutron cross sections are summarized in Table II, where they

are also compared with previous data. In the case of the $^{56}Fe(n,2n)^{55}Fe$ reaction, our data are seen to agree quite well with previous data by Wenusch[7], Frehaut[8], Molla[9], and Kozyr[10]. The measurement by Joensson et al.[11] is clearly much lower. In the case of the $^{63}Cu(n,p)^{63}Ni$ reaction, our measured cross section is lower than previous measurements. However, most of these cross sections are measurements of the total proton production which includes other possible reactions and hence are expected to be larger than our measurement. The measurement by Molla et al.[9], is directly comparable to ours since they measured the β^- activity from ^{63}Ni. However, their cross section has a relatively large uncertainty (40%) compared to our measurement (6.7%). No previous data were found for the $^{60}Ni(n,2n)^{59}Ni$ or $^{64}Ni(n,2n)^{63}Ni$ reactions.

Discussion and Conclusions

The measured neutron cross sections can be used to calculate the production of these long-lived activities in fusion reactor materials. Such calculations are needed to estimate radioactivity levels around fusion reactors and to determine the residual activities in waste materials. These techniques of chemical separations and liquid scintillation spectral analysis, backed by gamma and x-ray spectroscopy, have proven to be quite successful in the measurement of weak, long-lived activities, and we plan to study other such reactions in the future. Measurements are now in progess for the reactions $^{14}N(n,p)^{14}C$ (5700 y), $^{94}Mo(n,2n)^{93}Mo$ (3500 y), $^{94}Zr(n,2n)^{93}Zr$ ($1.5x10^6$ y), and $^{93}Nb(n,n')^{93m}Nb$ (13.6 y).

Acknowledgements

This work was supported by developmental funding from the Analytical Chemistry Laboratory at Argonne and by the Office of Fusion Energy, U. S. Department of Energy. We would also like to thank the staff of the RTNS II facility and Dr. D. W. Kneff of Rockwell International, Canoga Park, CA for assisting with the neutron irradiations.

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Table I

Results for $^{56}Fe(n,2n)^{55}Fe$

Sample	Energy[a] MeV	Fluence 10^{17}n/cm^2	At. Ratio 10^{-8}	σ mb[b]
^{56}Fe-1	14.83	1.88	8.58	456.
^{56}Fe-2	14.82	1.61	7.34	456.
^{56}Fe-3	14.85	1.31	5.86	448.
Fe-1	14.68	10.30	48.6	472.
Fe-2	14.81	4.53	19.9	440.

Results for $^{63}Cu(n,p)^{63}Ni$

Sample	Energy[a] MeV	Fluence 10^{17}n/cm^2	At. Ratio 10^{-8}	σ mb[c]
Cu-1	14.65	1.17	6.40	54.7
Cu-2	14.65	1.14	6.16	54.0
Cu-3	14.82	0.462	2.45	53.0

Results for $^{64}Ni(n,2n)^{63}Ni$

Sample	Energy[a] MeV	Fluence 10^{17}n/cm^2	At. Ratio 10^{-7}	σ mb[c]
^{64}Ni-1	14.85	1.96	1.90	967.
^{64}Ni-2	14.83	1.65	1.57	948.

Results for $^{60}Ni(n,2n)^{59}Ni$

Sample	Energy[a] MeV	Fluence 10^{17}n/cm^2	At. Ratio 10^{-8}	σ mb[d]
^{60}Ni-1	14.81	1.26	1.57	124±9
^{60}Ni-2	14.83	1.78	1.73	97±6
^{60}Ni-3	14.82	1.34	0.95	84±9

[a]Mean energy; width ≈0.5 MeV

[b]Uncert.: Stat. 1%, eff. 3%, std. 5%, $T_{1/2}$ 1.1%, fluence 5%, net 7.8%

[c]Uncert.: Stat. 1%, eff. 3%, std. 2.5%, $T_{1/2}$ 2.0%, fluence 5%, net 6.7%

[d]Uncert.: Stat. above, eff. 4%, $T_{1/2}$ 17%, fluence 5%, net 19-23%

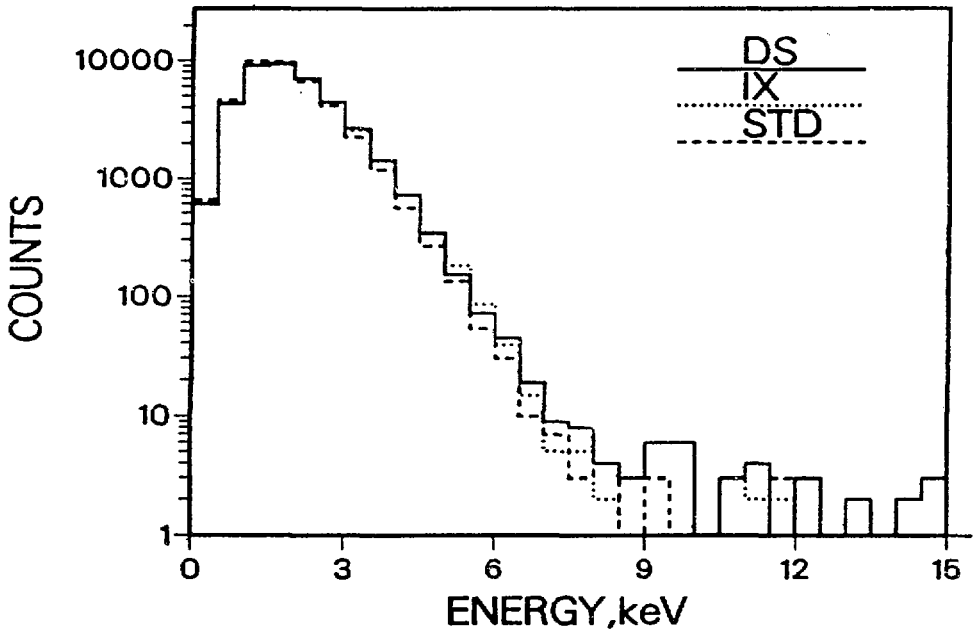
Table II
Summary and Comparison of Results with Previous Data

Reaction	Present E_n	Present σ,mb	Previous E_n	Previous σ,mb	Ref.
$^{56}Fe(n,2n)^{55}Fe$	14.8	454±35	14.0	440±90	7
			14.3	410±33	8
			14.7	440±40	9
			14.6	480±50	10
			15.1	190±40	11
$^{63}Cu(n,p)^{63}Ni$	14.7	54±4	14.7	125±50	9
$^{63}Cu(n,px)^{a}$			14.0	105±9	12
			14.1	149±30	13
$^{64}Ni(n,2n)^{63}Ni$	14.8	958±64		none	
$^{60}Ni(n,2n)^{59}Ni$	14.8	104±25		none	

[a]Total proton yield from ^{63}Cu includes other reactions

Figure Captions

1. Liquid scintillation spectra for ^{55}Fe from the $^{56}Fe(n,2n)$ reaction: The initial dissolution (DS); the ion-exchanged solution (IX); and the ^{55}Fe standard (STD).
2. Liquid scintillation spectra for ^{63}Ni from the $^{63}Cu(n,p)$ and $^{64}Ni(n,2n)$ reactions: The initial dissolutions (DS); ion-exchange products (IX); and ^{63}Ni standard (STD).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6
9
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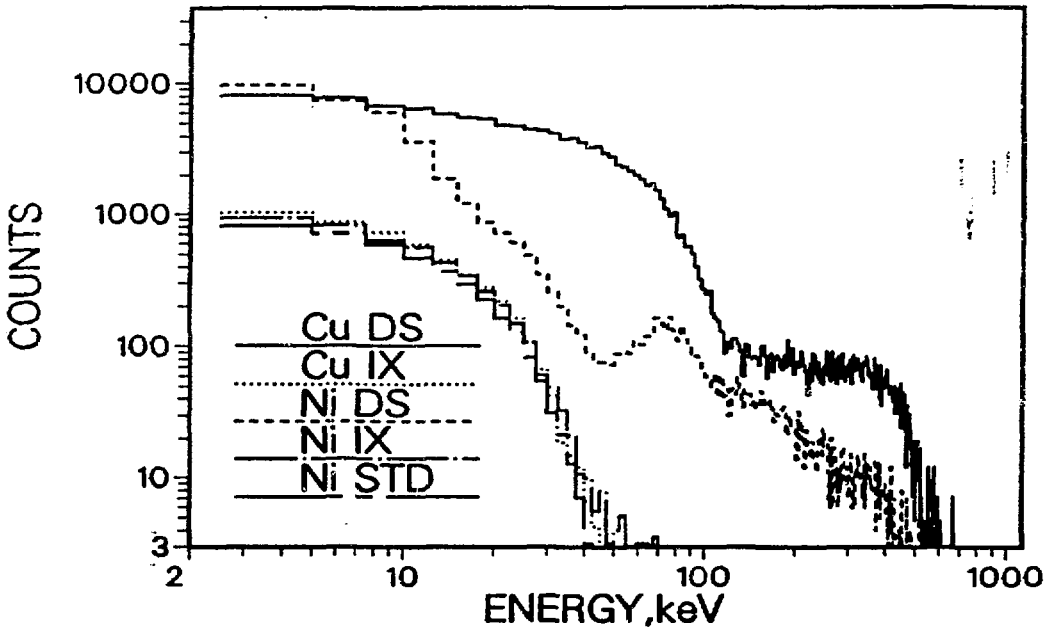
ENERGY,keV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ENERGY,keV
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Cu IX
Ni DS
Ni IX
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