Elements 99 and 100 from Pile-Irradiated Plutonium*

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THIS note[1] describes some nuclear and chemical properties of elements 99 [2] and 100. The transcalifornium elements were produced in a pile irradiation of plutonium (integrated flux of 1.0×10^{22} neutrons) in the Materials Testing Reactor. The purified transcurium elements were separated from each other with a Dowex 50 cation citrate column.[3] The final element-99 peak (Fig. 1) contained a total of 3.3×10^4 alpha disintegrations/minute. The energy of the prominent alpha group was measured by pulse analysis to be 6.64 Mev. The alpha spectrum of this isotope appears to exhibit fine structure which is characteristic for odd-even nuclides, e.g., similar to Np^{237} and Am^{241}. In the final californium peak were 2.3×10^5 alpha disintegrations/minute as well as 4.6×10^3 spontaneous fission disintegrations/minute. Alpha pulse analysis of the californium fraction showed at least two alpha groups of 6.01 and 6.10 Mev. These alpha groups chemically follow the large spontaneous fission activity as shown in Fig. 1 and are in the ratio of forty-five californium alpha disintegrations to one spontaneous fission disintegration. The presence of short spontaneous fission half-lives in the californium fraction is supporting evidence for the recently published spontaneous fission systematics.[4]

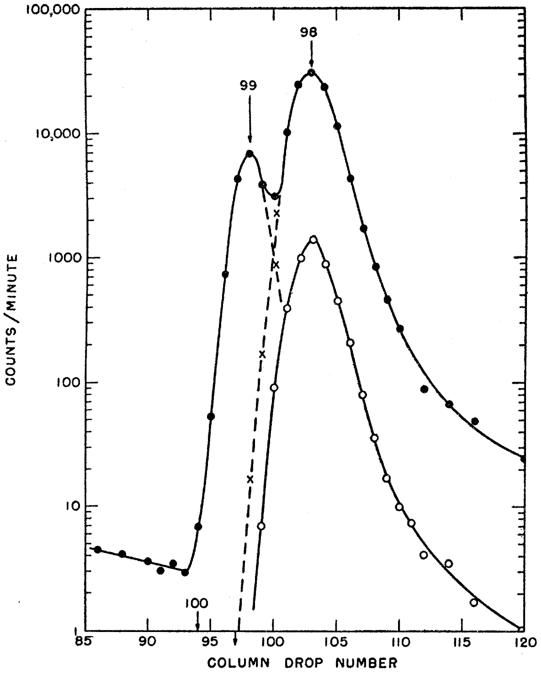

FIG. 1. The solid points represent the total activity in counts/minute (alpha particles plus spontaneous fissions) of successive drops from the Dowex 50 cation citrate column. The open circles give the spontaneous fissions in counts/minute as a function of drop number. The dashed lines give the respective amounts of californium and element-99 activities in the drops which contain alpha activity from both elements. The curium began to elute at drop 170 in this column run.

The small amount of spontaneous fission activity on plates containing the 6.64-Mev alpha particles is a measure of the excellent separation of element 99 from 98 (see Fig. 1). Drop 97 contained 8600 disintegrations/minute of 6.64-Mev alpha particles and about 0.004±0.002 fission disintegrations/minute. Assigning all of the fissions to californium gives a limit of 0.2 disintegrations/minute of californium alpha particles on the above plate.

The observed half-life of the 6.64-Mev alpha-emitting isotope of element 99 is 20±2 days (the decay was over a period of 8 days). By using a 20-day decay half-life for the above element-99 isotope, the spontaneous fission half-life is calculated to be greater than 10^5 years. This half-life limit can be increased if the spontaneous fissions do not decay with the 6.64-Mev alphas. Such a long spontaneous fission half-life (compared to even-even nuclides) for a 99 isotope is consistent with expectations for an odd-Z element. The 6.64-Mev alpha has grown in drop 109 from 2 counts/minute (at the time of the first alpha pulse analysis) to 13 counts/minute in six days, establishing its genetic relationship to californium. A number of arguments[1] indicate that the probable mass assignment of the element-99 isotope is 253.

Alpha pulse analysis showed the presence of an energy group of 7.20 Mev and possibly another group (one-third the abundance of the 7.20-Mev group) approximately 170 kev lower in energy in the element-99 fraction. From the energies of these groups one may deduce that they represent isotopes of $Z>99$ in equilibrium with β^--emitting element-99 isotopes. The ratio of 6.64-Mev activity to the 7.20-Mev activity is about 5000. An alpha group of approximately 7.1 Mev was shown to elute from a Dowex 50 cation citrate column ahead of the 6.64-Mev alpha group, which is evidence for assigning at least one of the energetic groups to element 100. The short half-life of the ~7.1-Mev alpha group which eluted ahead of element 99 prevented a possible resolution of this group in the absence of the element-99 activity.

Several chemical experiments on elements 99 and 100, in addition to the previously mentioned cation citrate elution behavior, have been performed. Both elements carry on LaF_3 and $La(OH)_3$, and solvent extract into tributyl phosphate from a highly salted, dilute nitric acid solution. In concentrated hydrochloric acid, element 99 behaves like curium with both Dowex A-1 anion and Dowex 50 cation resins.

The valuable assistance in these experiments by C. H. Youngquist, R. K. Sjoblom, James Gindler, and D. W. Engelkemeir is gratefully acknowledged. We also wish to thank W. M. Manning for guidance and many stimulating discussions.

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* These elements (99 and 100) have previously been discovered in other work at Argonne National Laboratory, University of California Radiation Laboratory, and Los Alamos Scientific Laboratory, not yet published.

[1] A manuscript containing details of these experiments as well as a number of additional experiments is in preparation.

[2] The production of lighter isotopes of element 99 by nitrogen-ion bombardment of uranium has recently been described: Ghiorso, Harvey, Rossi, and Thompson, Phys. Rev. 93, 257 (1954).

[3] B. H. Ketelle and G. E. Boyd, J. Am. Chem. Soc. 69, 2800 (1947); K. Street, Jr., and G. T. Seaborg, J. Am. Chem. Soc. 72, 2790 (1950).

[4] J. R. Huizenga, Phys. Rev. (to be published).

The Nuclear Spin of Si^{29}†

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SEVERAL attempts have been made to determine the spin of Si^{29} with either inconclusive,[1] conflicting,[2] or rather indirect[3] results. The consensus favors the value 1/2. Nuclear shell theory gives 1/2, 3/2, and 5/2 as the only possibilities.[1] We have eliminated values greater than 1, thereby establishing the spin of Si^{29} as 1/2. This was accomplished by resolving the multiplet structure produced in the fluorine nuclear magnetic resonance by the electron coupled interaction[4] of the Si^{29} spin with the F^{19} spins, using isotopically enriched $Si^{29}F_4$.

In pure liquid or gaseous $Si^{29}F_4$, the fluorine resonance should be a multiplet, with $2I(Si^{29})+1$ equally spaced components of the same intensity.[4] The SiF_4 actually used was prepared[5] from a sample of SiO_2 whose composition was given as 30, 69, and 1 percent, respectively, of Si^{28}, Si^{29}, and Si^{30}. The enriched sample of SiO_2 was supplied by the Oak Ridge National Laboratory. The spins of Si^{28} and Si^{30} are presumably zero so the $Si^{28}F_4$ and $Si^{30}F_4$ should give a single fluorine resonance with 31 percent of the total absorption, located at the center of the $Si^{29}F_4$ multiplet. The high-resolution spectrometer and experimental procedures used have been described elsewhere.[6] A typical oscilloscope photograph of the fluorine resonance observed in the liquefied sample of SiF_4 is reproduced in Fig. 1.

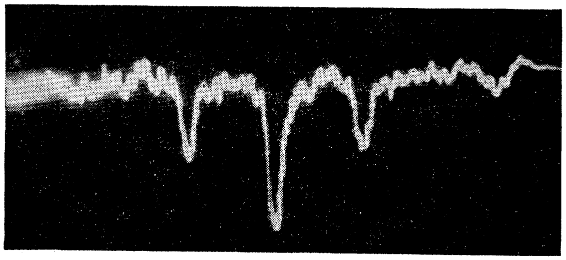

FIG. 1. The F^{19} nuclear magnetic resonance in a mixture of $Si^{28}F_4$ and $Si^{29}F_4$. The center line is from the $Si^{28}F_4$. The two outer lines are from the $Si^{29}F_4$; their separation is 46 milligauss. A sawtooth sweep of 135 milligauss was used; the pip on the far right is from the return trace.

Figure 1 shows a symmetrical multiple resonance of three components with approximate *peak* intensities of 1:2:1. The separation of the two outer components is 46 milligauss. The number of lines observed is compatible with a spin of either 1/2 or 1. For a spin of 1/2 the predicted *integrated* absorption of the components should be 34.5:31:34.5, and for a spin of 1, 23:54:23; in the latter case the $Si^{28}F_4$ and $Si^{30}F_4$ lines overlap the center component of the $Si^{29}F_4$ triplet. The observed *peak* intensities correspond more closely to the spin 1 case than to the spin 1/2. However, a spin of 1 is eliminated by the shell theory; moreover, there is a convenient mechanism to explain the intensities observed.

In aqueous, concentrated $H_2Si^{29}F_6$ the fluorine resonance was not split by the Si^{29} spin but was broadened to about 4 milligauss compared to 2 milligauss in $H_2Si^{28}F_6$. This effect[4] is produced most likely by fast chemical exchange[7] involving the fluorines. In the case of SiF_4, hydrolysis would result from a trace of water, giving HF which would catalyze exchange of the fluorines. Depending upon the exchange rate, there can be a significant reduction in the peak intensities and some broadening of the component lines. In Fig. 1 noise obscures any broadening of the outer components, but this explanation is supported by the observation that the ratio of the intensity of the outer components to that of the center line decreased at higher temperatures, for which chemical exchange would be faster. The isotopic composition of the SiF_4 was checked by an infrared analysis which gave 28 ± 2 percent $Si^{28}F_4$.

Figure 1 suggests an amusing and direct way to set an experimental maximum for the gyomagnetic ratio of Si^{28}. The splitting in gauss of the fluorine resonance in Si^AF_4 is given as[4] $\delta H = C\gamma \times (Si^A)/\hbar$, where C is a constant determined by the electronic structure of SiF_4. The central component in Fig. 1 is from the $Si^{28}F_4$ and splitting of it greater than 2 milligauss would be discernible. If we take the ratio of the equations for the splitting in $Si^{28}F_4$ and $Si^{29}F_4$, introduce the values of 2 and 46 milligauss for the splitting and the experimental value[1] for $\gamma(Si^{29})$, we find $\gamma(Si^{28}) < 0.05$. This value could be improved by taking greater pains to obtain maximum resolution and to minimize the effects of chemical exchange. Similar experiments are feasible in several other cases, including $C^{12}H_4 - C^{13}H_4$ and $H_2S^{32} - H_2S^{33}$ mixtures.

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[1] H. E. Weaver, Phys. Rev. **89**, 923 (1953).

[2] R. H. Sands and G. E. Pake, Phys. Rev. **89**, 896 (1953).

[3] R. L. White and C. H. Townes, Phys. Rev. **92**, 1256 (1953).

[4] Gutowsky, McCall, and Slichter, J. Chem. Phys. **21**, 279 (1953).

[5] C. J. Hoffman and H. S. Gutowsky, Inorg. Syntheses **4**, 145 (1953).

[6] Gutowsky, Meyer, and McClure, Rev. Sci. Instr. **24**, 644 (1953).

[7] H. S. Gutowsky and A. Saika, J. Chem. Phys. **21**, 1688 (1953).

Nuclear Induction with Separate Regions of Excitation and Detection

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A FEW years ago Purcell[1] pointed out the possibility of a nuclear induction experiment in which the sample is a flowing stream of water and the detection occurs at a location downstream of the region of excitation. More recently Benedek,[2] working under the direction of Purcell, investigated this possibility and in an unpublished report derived the expected form of the signal in some detail, as well as listing experimental conditions which are required in order that a nuclear induction signal be obtained.

This letter reports the performance of such an experiment. The essential details of the nuclear induction head are shown in Fig. 1.

The block is milled (unhatched section) of a solid piece of aluminum, and the wall separating the exciting and detecting coils is $\frac{1}{8}$ inch thick, with a $\frac{1}{16}$-inch hole drilled through for the water tube. These dimensions were chosen with a mind to keeping the direct electromagnetic coupling from excitor to detector down to a low level. A 30-cycle/sec lock-in detecting system with a 1-cycle/sec band width was used, the modulation being obtained with two coils, one fastened on the bottom of the block, the other on a cover plate. Except for water and electrical lead-ins, the block and cover enclosed the system completely.

The details of the water system, made of Lucite, are: Distance between centers of excitor and detector coils $= \frac{1}{4}$ inch; inner diameter of excitor tube $= 0.016$ inch; inner diameter of detector tube $= 0.040$ inch.

The excitor and detector coils are closewound of 0.003-inch copper wire, have 20 turns, and diameters of 0.072 inch and 0.062 inch, respectively. They are matched to coaxial cables by use of the condenser-transformer networks shown in the diagram.

From the foregoing data, the effective detector sample volume is slightly greater than 10^{-3} cc.

With a flow rate of 0.6 cc/sec, and a resonant frequency of 15 Mc/sec, a signal-to-noise power ratio of roughly 50 db was obtained. With decreasing flow rates, the signal drops off rapidly, so that at a flow rate of 1 cc/min noise is definitely visible on the resonant response.

The shape of the resonance curves has not yet been interpreted on a theoretical basis. There are several factors which hinder this, among them being the complicated flow pattern caused by the abrupt change in tube diameter, and complications introduced by the 30-cycle/sec modulation frequency. The theoretical prediction of a signal frequency equal to the driving frequency rather than any dipole precession frequency determined by the magnetic field has been verified.

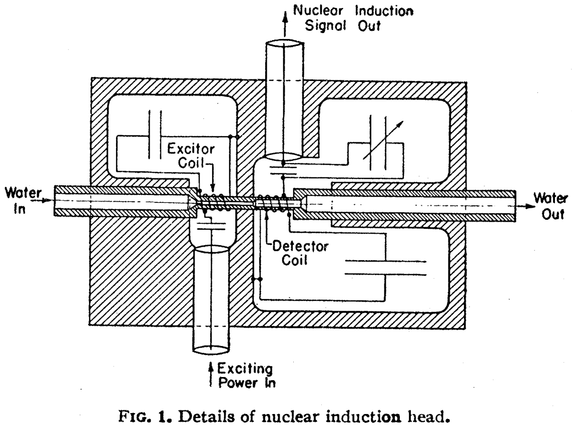
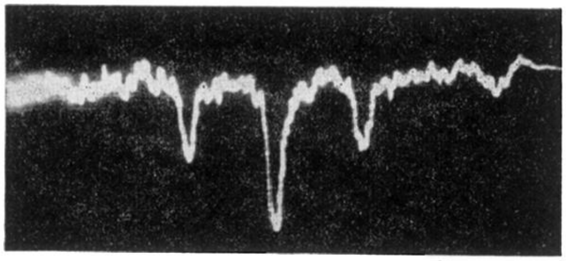


FIG. 1. Details of nuclear induction head.



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