Determination of the Cross Section for the Reactions $^{42}\text{Ca}(\text{n}, \text{p})^{42}\text{K}$ and $^{43}\text{Ca}(\text{n}, \text{p})^{43}\text{K}$ and Methods for Production of Carrier-Free Potassium Isotopes

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Dedicated to Professor Ole Lamm on his 60th birthday

The cross sections for the (n, p) reactions of ^{42}Ca and ^{43}Ca have been determined by reactor irradiation of CaCO_3 , carrier-free separation of potassium and comparison of the ^{42}K and ^{43}K activities with the activity of ^{24}Na obtained in a monitor of pure aluminium.

The measured cross sections were 2.1 ± 0.4 and 1.5 ± 0.3 mb for ^{42}Ca and ^{43}Ca respectively, the theoretically predicted ones, 1.3 and 4.5 mb.

The carrier-free separation method utilized included the following steps, (a) dissolution of the irradiated calcium carbonate in hydrochloric acid, (b) sorption of the calcium on Dowex A 1 chelating resin, (c) selective displacement of the potassium by means of ammonium chloride, (d) substitution of the chloride with hydroxide, on an anion exchanger, and (e) evaporation of the ammoniacal solution.

This separation method should also be suitable for the production of carrier-free ^{42}K or ^{43}K activities from enriched ^{42}Ca and ^{43}Ca , and make possible the recovery, with a high yield, of the expensive, enriched calcium isotopes. A fission neutron flux of $5 \times 10^{14} \text{ s}^{-1} \text{ cm}^{-2}$ should yield after one day's irradiation of 10 mg ^{42}Ca , about one mC of ^{43}K . Some advantages of carrier-free ^{43}K as compared with ordinary activated potassium are pointed out.

The neutron reaction denoted by (n, p) constitutes the standard method for the production of carrier-free activities of some important nuclides, *e.g.* ^{14}C , ^{32}P and ^{35}S . The cross sections for the reactions (n, p), (n, α) and also for (n, 2n) have been investigated for many nuclides for fission-spectrum neutrons, and in some cases several workers have studied the same cross section and arrived at more or less different results¹.

The theory presented by Hughes² made it possible to predict the cross section for a threshold reaction by simple calculations. Such calculations are

further simplified by a graphical method³, and at present a table of Q -values for (n, p) and (n, α) reactions for many nuclides throughout the periodic system is available, including also many experimental cross sections⁴. For nuclides of low atomic numbers, the Q -values for some other reactions (*e.g.* $(n, {}^3\text{He})$; (n, d) ; (n, t)) have also been published⁵.

In many cases the experimental cross section agrees fairly well with the predicted one, but in other cases, *e.g.* some titanium isotopes, the measured cross sections are one or two powers of ten lower than the theoretically calculated ones⁶.

The calculations mentioned are based on an analytical expression for the fission neutron spectrum, on the theoretical probability for a proton or alpha particle to penetrate the coulomb barrier around a nucleus, and on the "geometric" dimensions of the nucleus. The cross section is given as the mean cross section, calculated for the entire fission neutron spectrum.

In more elaborate calculations of cross sections it is necessary to take into account other factors, for instance competing reactions, energy level schemes of the reaction product nuclides and neutron penetrabilities. Nevertheless, experimental determination of cross sections will always be of value. From a nuclear science point of view, it would be more interesting to study the cross sections for discrete neutron energies, and this has been done especially for 14 MeV neutrons from accelerator sources, see for instance⁷ and⁸.

In the case of very small cross sections and long half-lives, however, it is often more convenient to determine the mean cross sections for fission neutron spectra by means of irradiation in a nuclear reactor, and the values thus obtained are also more relevant for the planning of reactor production or, for instance, when judging eventual interferences in activation analysis performed by reactor irradiation.

In the case of calcium, the (n, p) reactions of ${}^{40}\text{Ca}$ have been the subject of extensive calculations, partly based on theories and partly on experimental data⁹; the (n, p) reaction of ${}^{44}\text{Ca}$ has been recognized, studied and utilized to obtain ${}^{44}\text{K}$ activities for decay scheme studies^{10,11,12}; the corresponding reaction of ${}^{43}\text{Ca}$ is also mentioned¹³ and the one of ${}^{42}\text{Ca}$ has been studied¹⁴. However, no attempts seem to have been made to determine the experimental mean cross sections for (n, p) reactions of calcium isotopes, induced by fission spectrum neutrons. It seemed interesting, therefore, to make an effort to do so. This first experiment was planned to give, from the same irradiation and the same separation, the cross sections for the (n, p) reaction of both ${}^{42}\text{Ca}$ and ${}^{43}\text{Ca}$, because the induced activities, ${}^{42}\text{K}$ and ${}^{43}\text{K}$, have similar half-lives, 12.5 h and 22.4 h, respectively. Other potassium isotopes produced from calcium should not interfere in this case, because their half-lives are much longer (${}^{40}\text{K}$, half-life 10^9 years) or much shorter (${}^{44}\text{K}$, 22 m). There are natural calcium isotopes also available for the production of ${}^{46}\text{K}$ and ${}^{48}\text{K}$, which are both unknown so far, but it can be inferred from beta decay systematics that their half-lives ought to be negligibly small.

THEORETICAL INTERPRETATIONS. CHOICE OF EXPERIMENTAL CONDITIONS

1. *Nuclear considerations.* From the total disintegration energies of the β -decaying nuclides ^{42}K and ^{43}K and from the mass difference between the neutron and the proton, the Q -values of the reactions $^{42}\text{Ca} (n, p) ^{42}\text{K}$ and $^{43}\text{Ca} (n, p) ^{43}\text{K}$ were calculated. After correction for the kinetic energy transmitted to the compound nucleus by the impact with the neutron, the neutron threshold energies, E_t , were calculated. The effective threshold energies, E_{eff} , according to Hughes were derived from the graph in his book² and the mean cross sections, $\bar{\sigma}_{\text{theor.}}$, for fission neutron spectrum were obtained from Inthoffs graph³. All these values are tabulated in Table 1, together with the natural abundances for the target nuclides. In the same table are also included E_{eff}

Table 1. Threshold energies and theoretical cross sections for the (n, p) reaction of ^{42}Ca and ^{43}Ca , with calculated cross sections or Q -values for some other reactions of calcium isotopes, competing either with respect to the cross sections or with respect to the production of ^{42}K and ^{43}K .

Target nuclide	^{42}Ca	^{43}Ca	^{44}Ca
Abundance of target isotope	0.64 %	0.145 %	2.06 %
Product nuclide from (n, p)	^{42}K	^{43}K	^{44}K
Half-life of product nuclide	12.5 h	22.4 h	22 m
E_t , threshold energy for (n, p)	2.8 MeV	1.1 MeV	
E_{eff} , for (n, p) ²	6.4 MeV	4.7 MeV	
$\bar{\sigma}_{\text{theor.}}$ for (n, p)	1.3 mb	4.5 mb	
Q -value for $(n, 2n)$	-11.4 MeV	-8.05 MeV	
E_{eff} , for (n, α)	9.7 MeV	10.2 MeV	
$\bar{\sigma}_{\text{theor.}}$ for (n, α)	0.22 mb	0.13 mb	
Q -value for (n, d) ⁵		-8.5 MeV	-9.9 MeV
Q -value for (n, t) ⁵			-13.3 MeV

and $\bar{\sigma}_{\text{theor.}}$ for (n, α) reactions, calculated in the same way as above except for the Q -values, which were obtained from the mass differences between reacting and resulting nuclides and particles. Also included are the Q -values for the $(n, 2n)$ reactions, calculated in the same way as for the (n, α) reactions together with Q -values for (n, d) and (n, t) taken from Ref.⁵, in order to facilitate a judgement of the competition of these reactions with the (n, p) reactions.

Data for the calculations mentioned were taken from standard compilations^{15,16}.

From a nuclear spectroscopic point of view, the decay schemes of ^{42}K and ^{43}K are very well known^{17,18} and the possibility of detection, identification and quantitative estimation of each of ^{42}K and ^{43}K in the presence of rather large activities of the other by means of gamma spectrometry is obvious with the exception that too high ^{42}K activities might mask the ^{43}K spectrum by the Compton, backscatter and Bremsstrahlung distributions.

2. *Chemical considerations.* When the cross section for a nuclear reaction is to be deduced from the induced activity, it is necessary to avoid, or take into account, the presence of nuclides which may, through other reactions, contribute to the same activity. In addition, although modern gamma spectro-

meter equipment often permits exclusive measurement of a given gamma energy in presence of others, foreign activities are likely to diminish the significance levels both in the qualitative identification and in the quantitative estimation. Hence, the growth of undesirable activities must be suppressed and a chemically pure target must be utilized. However, the purity of practically obtainable chemicals is limited, and very low contents of impurities with high activation cross sections might yield significant activities besides the interesting ones, because these are produced by low cross sections from isotopes of low abundances. Moreover, activities produced from other isotopes in the natural target element must be taken into account, *e.g.* ^{47}Ca and its daughter nuclide ^{47}Sc . Therefore it was decided to separate the alkali ions as one group from all other elements in the irradiated matter. With a successful separation method, the demand for ultimate purity of the target should then mainly be restricted to the alkalis and the actual target material was specifically processed for this purpose.

By removing the alkalis, the risk for irrelevant ^{42}K activities produced by neutron capture in ^{41}K is suppressed correspondingly. Other chemical sources for ^{42}K and ^{43}K activities will be mentioned under "discussion".

As for the chemical form of the target, it ought to be easily dissolvable and its anion should not give rise to activities contributing significantly to the dose rate level during the separation process after the irradiation. Further, the anion should not complicate the separation steps.

EXPERIMENTAL

1. *Preparation of the target substance.* The target substance was prepared from an analytical grade of calcium nitrate (Merck). An attempt was made to remove or diminish the alkali element impurities from the calcium by dissolving the salt in water, sorbing the calcium ions in a Dowex A 1 chelating resin and displacing the alkalis selectively by means of an alkali-free ammonium chloride solution.

The exchanging groups of the Dowex A 1 resin are nitrilodiacetate groups on a conventional divinylbenzene-styrene copolymer matrix¹⁹. By chelating effects this resin takes up bi- and polyvalent cations very selectively in presence of alkali ions, and therefore any of the alkalis can be selectively displaced by means of another monovalent cation²⁰, in the present case by ammonium. Also, the differences in stability constants for different chelated cations can be utilized for their separation²¹.

The Dowex A 1 available to the author at the time of this experiment was a 50–100 mesh technical grade, containing many "dirty" particles with different appearances. It was therefore purified by back washing the fines, and the dirty-looking particles were removed fraction after fraction by suspending the exchanger in a mixture of trichloroethylene and ethyl alcohol and adjusting the mixture to a density slightly larger or smaller than the density of the main exchanger grains in that solvent, and leaving it overnight to separate. This was done with the exchanger firstly in the shrunk hydrogen form, secondly in the swollen ammonium form, and thirdly in the shrunk copper form. In each case a certain fraction of dark or oily particles together with some ordinary-looking exchanger separated from the bulk of the material. After this treatment the remaining exchanger looked and behaved very homogeneously.

The purified exchanger was packed in a polymethylmethacrylate column after displacing the other solvents by water. The copper was displaced by one-molar hydrogen chloride, and the resin was then saturated with ammonium from an ammonia solution.

Because a faint blue, copper chelate colour seemed to remain in the exchanger when the hydrogen and ammonia steps were performed at rates normal for cation exchangers

of the sulphonate types, these two cycles were repeated, this completely removed all visible copper colour. The kinetics of ion exchange in Dowex A 1 are known from other studies to be slow²². Because of the swelling properties of the Dowex A 1 resin, the ammonia saturations were performed by upwards flow.

The ammonium ions in the exchanger column were now substituted with calcium ions from an aqueous solution of calcium nitrate, and any alkali metals in the resin were displaced by a slightly ammonical, half-molar solution of ammonium chloride. Because the alkali content of this solution would set a theoretical limit for the resulting alkali level in the exchanger, it was prepared by passing distilled water through a mixed-resin bed and dissolving gaseous hydrogen chloride and gaseous ammonia in it. All operations were performed in polyethylene equipment. In order to test the purity of the deionized water, it was passed through an electrical conductivity cell, directly from the exchanger column so that atmospheric carbon dioxide should not contribute to the results. The measured conductivity was 130 % higher than that calculated for pure water from the dissociation constant and equivalent conductance of hydrogen and hydroxide ions at the experimental temperature, 19.1°C. No attempts were made to obtain water of higher resistance.

The amounts of ammonium chloride passed through the chelating exchanger column corresponded to four times the total exchange capacity.

The column was then rinsed with two bed volumes of demineralized water, and the calcium was displaced by means of half-molar hydrogen chloride in demineralized water. The displacement from the two feet high column was performed in a couple of hours, and the first and last quarters of the calcium chloride in the effluent were rejected because impurities might have been enriched at either end.

The middle fraction was collected in a polyethylene beaker, and ammonia gas was absorbed to a concentration slightly higher than that of the chloride.

Finally, gaseous carbon dioxide was absorbed until neutralization against thymol blue. The precipitated calcium carbonate was filtered on a sintered glass filter, washed once with demineralized water and dried to constant weight at 110°C.

The yield was almost eight grams of calcium carbonate. Two polyethylene tubes were filled with this substance, slightly more than 2 grams in each, for irradiation.

2. *Irradiation.* One sample of calcium carbonate was wrapped in a 0.3 mm thick cadmium foil together with 0.5 g of spectrographically standardized aluminium (Johnson, Matthey & Co., Ltd., London), 0.5 g of magnesium sulphate, 10 mg of sodium acetate and 10 mg of potassium acetate. The three last-mentioned substances were of analytical grade and all were contained in their own polyethylene tubes. The magnesium and sodium contents of the aluminium were estimated to 10 and 2 ppm by the purchaser. All samples were placed close to the calcium carbonate, and the sodium acetate specially close to the aluminium sample. The assemblage was irradiated for 21.5 h in a central position in the Swedish reactor R 1, the nominal thermal neutron flux being $12 \times 10^{11} \text{ s}^{-1} \text{ cm}^{-2}$ and the expected flux of fast neutrons being almost one decade lower. The sodium salt was intended as a standard for the estimation of the impurity level of sodium in the calcium carbonate and also in the aluminium monitor, and the potassium salt served as a standard for the estimation of the potassium in the calcium carbonate. The sulphate was intended as a second neutron flux monitor.

In order to distinguish between the alkali activities induced by fast neutron activation of aluminium and calcium and the corresponding activities induced by neutron capture in the alkali impurities of the monitor and the target, a similar irradiation unit including calcium carbonate, aluminium, sodium and potassium acetates and without the cadmium shielding was irradiated during the last 16 3/4 hours of the irradiation time for the cadmium container and about 10 cm distant from it. Special care was taken in the packaging of the assemblage without cadmium to avoid too large errors from the thermal neutron flux gradient.

3. *Chemical separations of the irradiated targets.* The irradiated calcium carbonate samples were each dissolved in a small excess of hydrochloric acid. The solutions were neutralized to pH = 5 with ammonia and then passed into a Dowex A 1 column of 50 % higher capacity than the calcium amount. The exchanger was in the ammonium form, the interstitial solution pure water.

The activity of the effluent was monitored by means of a thin-window (1.4 mg/cm² mica) GM tube coupled to a counting ratemeter equipped with a recorder. The effluent

was passed through a flow cell, covered with a 0.6 mg/cm² film of chlorinated rubber and designed to make possible the detection of ⁴⁵Ca with a high efficiency yield.

The alkalis in the exchanger were now displaced with a half-molar ammonium chloride solution. An inspection by means of a GM tube of the longitudinal distribution of the beta activities in the column showed a peak below the calcium saturated region, which moved with the ammonium chloride solution in accordance with the expected behaviour of alkalis. The activity in the flow cell ascended to hundred times the background count rate when this peak passed, remained almost constant in an effluent volume corresponding to the excess capacity in the exchanger and descended steadily to the true background count rate ($\pm 20\%$). The volume containing this activity was collected as the fraction of interest.

After collection of the alkali activities, the calcium was displaced from the column with 0.2 M hydrochloric acid. Gamma spectrometry of all fractions of the effluent showed that no significant amounts of ⁴²K and ²⁴Na had been lost from the alkali fraction. The only additional gamma activity observed in these pure ⁴⁷Ca spectra was disregarding the growing ⁴⁷Sc peak, a small peak with an energy slightly below 0.4 MeV and a few hours half-life, probably due to strontium-87 m.

The ammonium chloride solution containing the potassium activities was passed through a column of Dowex 2 in the hydroxide form, with sufficient capacity to convert all the chloride to hydroxide. The ammonia effluent was evaporated under suction in a rotating evaporator to a volume of a couple of milliliters. The last evaporation, to dryness, was performed in a small beaker on a water bath. The total residue was estimated visually to be far less than one mg.

The residue was dissolved in a few drops of water and about half the solution was transferred with a micro pipet to a sulphonated spot on a polystyrene film²³, intended for 4 π beta counting. The polystyrene film (1.0 mg/cm²) was sulphonated by placing one drop of concentrated sulphuric acid on it for a short time. The sulphonated area was a little more than one cm in diameter, and was left in the hydrogen form after it had been rinsed with distilled water. The activity of the transferred sample was totally absorbed by ion exchange and was not removed when the spot was rinsed with water.

The exact fraction of the total potassium activity transferred to the polystyrene film was determined by gamma spectrometry. That no potassium activities were lost during the evaporation or other steps, was confirmed by careful monitoring of all the equipment.

In order to decrease the content of ²⁴Na in the sample for gamma spectrometry, the sample was diluted to 20 ml, potassium and some sodium carrier were added and the potassium was precipitated as tetraphenylboron²⁴ and taken on a filter paper. More potassium carrier was added to the filtrate, a new precipitation was performed in the same beaker and the slurry filtered on a new paper. The ⁴²K activity of the last precipitate was shown by gamma spectrometry to be only 5 % of the first. In view of the fact that the first precipitate was not quantitatively transferred to the filter paper, this should prove that all the potassium activity was retained in the filter cakes, the precipitation conditions being the same in both cases.

4. *Radioactivity measurements.* All gamma spectra except four were obtained by means of a 3" $\times$ 3" NaI (Tl) crystal and a multichannel analyzer of the Hutchinson-Scarrott type, used in a 78 channel mode. All samples were placed on the central axis of the detector, at measured distances from its face. The distances were referred to the geometrical centre of the active bodies. An 8 mm aluminium absorber was utilized for all measurements.

The irradiated standard alkali acetates were dissolved in 50 ml volumes of carrier solutions, and small measured volumes were transferred to matched polyethylene tubes and diluted to a certain mark on the tube. The potassium tetraphenylboron precipitates together with the filter papers were compressed to the same volume in a similar tube. The aluminium monitors were divided into smaller pieces and that one with the most suitable activity level was utilized for comparisons with the potassium activities. The fractions of the ²⁴Na activities utilized were determined by weighing, assuming that the self-shielding against fast neutrons and the gradients in the fast neutron flux were both negligible within 0.5 g of aluminium.

Besides the more familiar comparisons of the intensities of the same gamma energy from different samples, the purpose of the measurements was to compare the ²⁴Na activity in the aluminium sample with the ⁴³K and ⁴²K activities from the irradiated calcium.

Fig. 1. The decay scheme of ^{43}K according to Benzzer-Koller *et al.*¹⁷

The total disintegration rate of ^{42}K was calculated from the pulse rate under the 1.52 MeV photopeak, corrected for time resolution losses, for the total detection efficiency for this energy at the actual distance, 6.5 cm, for the peak to total ratio²⁵, and from the fact that the intensity of this transition is only 18 %.

The disintegration rate of ^{24}Na was determined in the same manner from the 1.37 MeV peak taking into account the losses from this peak due to coincidence with pulses from the coincident ($T_{1/2} = 2.5 \times 10^{-11}$ s) 2.75 MeV transition.

The decay scheme of ^{43}K (Fig. 1) is more complicated than those of ^{42}K and ^{24}Na and special care is necessary when its disintegration rate is determined. In Table 2 the different gamma energies from ^{43}K are tabulated together with their intensities¹⁷.

Table 2. Gamma transitions in the ^{43}K decay scheme according to Ref.¹⁷

Gamma transitions			Compound peaks	
Number	Energy MeV	Intensity (Emitted quanta per 100 disintegrating nuclei)	Approximate energy, MeV	Intensity
γ_1	0.220	3 ± 1	0.38	103 %
γ_2	0.371	85 ± 8		
γ_3	0.388	7 ± 1		
γ_4	0.394	11 ± 1		
γ_5	0.591	13 ± 1	0.61	94 %
γ_6	0.614	81 ± 8		
γ_7	1.005	2 ± 0.2		

A conventional gamma spectrometer with its limited energy resolution will see the gamma energies γ_2 , γ_3 and γ_4 as a somewhat broad, compound peak and γ_5 and γ_6 as another compound peak.

When the crystal is irradiated at a small solid angle from a ^{42}K source, the component intensities within each compound peak are additive, with 94 % as the resulting intensity at 0.61 MeV.

At the actual source-crystal distance, 6.5 cm, there are some coincidence gains and losses to account for. From Ref.¹⁷ it seems likely that all successive internal transitions have short enough half-lives to be coincident when measured with a NaI (Tl) crystal. The assumption is made that no successive gamma emissions are angularly correlated to any significant extent.

The fractional loss of counts from a certain gamma *peak* caused by another, coincident gamma emission is equal to the total detection efficiency for this other gamma energy, multiplied by the ratio between the rate of coincident emission and the rate of emission of the gamma energy being studied. The contribution to a peak from two coincident gamma emissions with a suitable energy sum is calculated in the same way as the count losses, except that also the peak-to-total ratio must be taken into account.

In Table 3 are given the peak efficiencies for the actual energies calculated from the total detection efficiencies and peak-to-total ratios as interpolated from the graphs given in reference ²⁵.

Table 4 shows the calculated losses and gains to and from other parts of the ^{42}K spectrum for the 0.61 MeV compound peak. Second-order terms were not taken into account. The resulting value was used to calculate the disintegration rate of ^{42}K in the source.

When the ^{42}K activity had decayed to an inconveniently low level for external measurements, its spectrum was recorded by means of 256 channel Nuclear Data Analyzer and a $3'' \times 3''$ NaI (Tl) well crystal. The counting time was 60 min., and four spectra were taken at one-day intervals.

The decay of the activities on the polystyrene film was followed by means of a Baird Atomic 4 π proportional counter, and a fraction of the ^{32}P activity separated from the irradiated magnesium sulphate was mounted on a similar (1 mg/cm²) film and measured in the same counter.

Table 3. γ -Detection efficiencies at 6.5 cm distance from a $3'' \times 3''$ NaI (Tl) crystal ²⁵.

γ -Energy	Nuclide	Total efficiency	Peak/Total	Peak efficiency
1.52	^{42}K	0.0297	0.313	0.0093
1.37	^{24}Na	0.0306	0.335	0.0102
0.61	^{42}K	0.039	0.57	0.0222
0.38	^{42}K	0.046	0.755	0.035
0.22	^{42}K	0.055	0.910	0.050

Table 4. Detection efficiency for the 0.61 MeV compound peak of ^{42}K at 6.5 cm distance from a $3'' \times 3''$ NaI (Tl) crystal, with corrections for coincidence gains and losses:

"Main" γ	Coinc. γ	Probable number of coincident emissions per 100 "main" gammas	Contributions to the 0.61 MeV peak efficiency, pulses per 100 decaying nuclei
γ_6			0.180
γ_6	γ_3	7.5	—0.0006
γ_6	γ_2	100	—0.008
γ_5			0.029
γ_5	γ_3	6.3	—0.0001
γ_5	γ_4	85	—0.0011
γ_1	γ_2	90	0.0047
γ_1	γ_3	6.3	0.0003
γ_1	γ_4	85	0.0044
			Total 0.209

RESULTS

Gamma spectra were first taken of the irradiated but unseparated samples, and the following results for ^{24}Na were obtained from the 2.75 MeV peak of these spectra.

The ^{24}Na activity calculated for 1 g of the cadmium shielded aluminium, equaled the activity from 77 μg of sodium from the acetate standard. According to the spectrographically estimated sodium content in the aluminium, 2 ppm, 97 % of the ^{24}Na activity in aluminium originated from the (n, α) process.

The count rate per gram of the unshielded aluminium, for the peak at 2.75 MeV, was 1.7 ± 0.9 % higher than the corresponding value for the shielded material. The uncertainty given being the standard deviation from the counting statistics only.

The sodium content of the calcium carbonate was calculated to be 3.0 ppm from the cadmium shielded sample and 2.5 ppm from the unshielded one. The first value is assumed to be the most reliable one because the sodium standards were assymmetrically located with respect to the carbonates and the gradient of the thermal neutron flux was unknown.

Fig. 2 shows a spectrum of the potassium tetraphenylboron precipitate 33 h after the irradiation. Also shown, is a part of another spectrum obtained under equal conditions of the same activity, but prior to the precipitation. The inserted spectrum was normalized to fit the ^{42}K peak.

Three gamma spectra of the potassium activities separated from the unshielded target were obtained on the first, second and third days after irradiation. The conditions of measurement were the same as for the spectrum in Fig. 2 and the spectral shape the same except for the 1.37 MeV peak from ^{24}Na which revealed a few tenths higher intensity than the peak inserted on Fig. 2. The small effect on the activation of sodium from the cadmium shield is consistent with the large resonance cross section for neutrons of 2.85 keV energy ²⁶.

The ^{24}Na peak was quantitatively identified by its half-life and by comparison with the peak at 2.75 MeV (from another spectrum) and the spectrum of the standard sodium salt.

The ^{42}K peak was identified by its energy (within ± 2 % from the peak of the standard potassium salt) and its half-life ²⁷.

The energies of the peaks I and II in Fig. 2 were found to be 0.39 ± 0.02 MeV and 0.61 ± 0.03 MeV, by interpolation between peaks from ^{57}Co and ^{22}Na . Both peaks decayed with a half-life of 22 ± 2 days.

The potassium tetraphenylboron precipitate was analyzed in the well type crystal on the third day after irradiation and on the three succeeding days. The first of these spectra is shown in Fig. 3. The peak numbered III is the sum peak of components from the ^{43}K compound peaks I and II. The half-life of each of these three peaks was calculated to be 23.3 ± 1.2 ; 22.7 ± 1.2 and 23.2 ± 1.5 days, respectively.

The profile of the valley between peak II and peak III maintained its form during the decay and is assumed to origin from secondary effects (compton or backscatter) from ^{43}K activity. The peak at 1.3 MeV and the one at 0.16 MeV decayed with half-lives of a few days, high error and unknown

Fig. 2. Spectrum of the precipitated potassium activities obtained 33 h after irradiation at 6.5 cm distance from a 3" $\times$ 3" NaI (Tl) scintillation detector with an 8 mm Al absorber. I and II are the ^{43}K compound peaks at 0.38 and 0.61 MeV, IV is the 1.52 MeV peak from ^{44}K . The inserted part indicates the ^{24}Na activity of the sample before precipitation.

Fig. 3. Spectrum of the same sample as in Fig. 2, obtained by a 3" $\times$ 3" well type crystal. Peak numbers are the same as in Fig. 2, III is the sum peak of components from peak I and II.

background level prohibiting exact half-life determinations. From nucleogenetic points of view, ^{47}Ca and its daughter nuclide ^{47}Sc are assumed to be responsible for those peaks.

The ratio between the count rates for peak IV and II (see Fig. 2) for the potassium from the shielded target agreed, within the error limits, with the same ratio for the unshielded target, when corrected for the difference in irradiation times. Because the fission neutron flux was the same in both cases, the potassium content of the target substance was too low to be detected.

The ^{42}K activity per gram of the shielded calcium carbonate matched the activity from 8.5 μg of potassium in the standard. The limit for the potassium impurity deduced from these results is 0.5 ppm.

Finally, the cross sections for the (n, p) reactions of ^{42}Ca and ^{43}Ca were calculated from the count rates under the gamma peaks at 0.61 (^{43}K), 1.37 (^{24}Na) and 1.52 MeV (^{42}K), assuming a value of 0.56 mb for the reaction ^{27}Al (n, α) ^{24}Na ²⁸.

For the calculation of the cross sections, the following factors were taken into account for each of the nuclides: amount of target nuclide irradiated, build up during irradiation and decay after it, decay scheme, detection effi-

ciency, absorption and dead time losses and the fraction of the total activity being analyzed.

The resulting cross sections for a fission neutron spectrum were for ^{42}Ca (n, p) ^{42}K : 2.1 ± 0.4 mb and for ^{43}Ca (n, p) ^{43}K : 1.5 ± 0.3 mb.

The ^{42}K (and ^{24}Na) activity in the β -source prohibited the isolation of the 22.4 h activity before it had decayed to a very low level. The cross sections calculated from a comparison with the count rate for the ^{32}P activity, assuming a cross sections of 60 mb²⁸ for the reactions ^{32}S (n, p) ^{32}P , agreed well with the cross sections obtained by means of gamma spectrometry. However, an uncertainty factor of two must be ascribed to this determination, and this uncertainty is based on the assumptions of the author rather than on a mathematical analysis.

DISCUSSION

The experimental cross sections for neutron threshold reactions found in the literature often deviate appreciably from one determination to another, for instance the values for ^{32}S (n, p) ^{32}P range from 154 to 21 mb⁴. When a threshold reaction is used to monitor the flux of fast neutrons, the result is obviously dependant on the reliability of the cross section of the monitor. In this case the value suggested by Mellish²⁸, 0.56 mb for ^{28}Al (n, α) ^{24}Na , was assumed as the reference.

A source of error in such determinations is the deviation from a true fission spectrum at the irradiation position²⁹. Errors of this sort should be at a minimum, however, when the effective threshold energies, E_{eff} , for the monitor and the studied reaction match each other, as is nearly the case here.

Errors from flux fluctuations are negligible if the irradiation time is short in comparison with the half-lives or else when the activities from the target and the monitor have nearly the same half-life, as do ^{42}K and ^{24}Na . Errors of this type are likely to be negligible also in the case of ^{43}K .

The errors in gamma detection efficiencies have not been critically studied by the author, but they are assumed to cancel, especially in the case of energies of the same magnitude (^{42}K and ^{24}Na).

The small abundances of the target isotopes and the small cross sections studied make it necessary to discuss other possible nuclear reactions which might also result in the activities being studied. The case of ^{41}K (n, γ) ^{42}K has been mentioned under "results". ^{45}Sc might by an (n, α) reaction give ^{42}K . The cross section for this reaction is less than 5 mb⁴, the content of scandium should according to the analysis of the calcium nitrate be less than 0.001 % and the scandium might have been depleted but not enriched during the chemical preparations of the target. The product (< 5) mb times (< 0.006) % has thus to be compared with 2 mb times 0.6 %, and a contribution to the ^{42}K activity from scandium can thus be disregarded. It seems justified to neglect, in the same way, the ^{45}Sc (n, ^3He) ^{43}K reaction, because the Q -value of this reaction is -1.7 MeV against -0.4 MeV for ^{45}Sc (n, α) ^{42}K ⁵.

^{44}Ca has higher abundance than ^{43}Ca , and could give ^{43}K by a (n, d) reaction. However, the Q -value of this and other (n, d) and (n, t) reactions presented in Table 1 indicate that their contribution to the ^{42}K and ^{43}K activities should be negligible.

Other types of error are mentioned under "results". The errors given for the final cross section values are not strictly mathematically deduced, as allowance was made for some systematic errors within the limits. The author is convinced that the errors should match a confidence level of at least 90 %, if the utilized values for the monitor cross section and the gamma intensities from ^{43}K are correct.

It is obvious that practically, carrier-free activities of ^{42}K and ^{43}K can be produced by the methods utilized in the present study. The ^{24}Na activity present could be diminished either by preparation of a purer target, by a sodium shield around the target (for absorption of neutrons of the resonance energy for ^{23}Na) or by separation of the sodium and potassium activities, for instance by means of a crystal ion exchanger³⁰. In the last case, contamination of for instance ^{47}Ca and the grown in ^{47}Sc could also be more quantitatively eliminated. The availability of potassium isotopes of higher specific activities than those obtainable through (n, γ) activation of natural potassium is likely to be of value, for instance, for labelling of red corpuscles^{31,32} or for studies of ion transport in heart muscles³³.

However, when corrections for decay or absorption must be applied, it is much more convenient to have a radiochemically pure activity.

^{43}K has for most purposes many advantages in comparison with ^{42}K , e.g., longer half-life, much lower mean β energy, lower γ energies (higher detection efficiency) and much higher γ intensities. These circumstances make it preferable for autoradiographic purposes and for in vivo experiments where the dose rates are critical. ^{43}K has been suggested by Ullberg³⁴ for studies of differences in the distribution of cesium and potassium in animals by means of double-tracer autoradiography.

^{43}K has earlier been detected as a spallation product³⁵ and it has been produced from argon: $^{40}\text{Ar} (\alpha, p) ^{43}\text{K}$ ^{36,17,37,38}.

In order to obtain a radiochemically pure ^{43}K activity in a nuclear reactor, enriched ^{43}Ca targets must be utilized. With a cross section of 1.5 mb it should be possible to obtain after irradiation of 10 mg of ^{43}Ca for one day in a fission neutron flux of $5 \times 10^{14} \text{ s}^{-1} \text{ cm}^{-2}$, one millicurie of carrier-free ^{43}K .

By slight modifications of the method utilized here for the purification of the calcium target, it should be possible to recover, with a high yield, the expensive, enriched calcium isotope.

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