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SUBJECT: Determination of Li^6 in Aqueous Solution by Neutron Activation Analysis

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Abstract

A method for determining the concentration of Li^6 in aqueous solution has been tested using the nuclear reactions $Li^6(n,\alpha)H^3$ and $O^{16}(H^3,n)F^{18}$. Annihilation γ radiation of induced 1.87 hour F^{18} radioactivity was counted with a well-type scintillation counter, and the radioactivity per millimole of lithium was found to be independent of lithium concentration below about 0.2 moles/liter. The sensitivity limit for detecting lithium is less than 0.1 micromole (0.0075 micromole Li^6).

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DISCLAIMER

Introduction

Osmond and Smales[1], Smales and Webster[2], and Leddicotte and Bate[3] have suggested that Li^6 may be determined by measuring the induced F^{18} radioactivity produced in a neutron-irradiated sample by the nuclear reactions $Li^6(n,\alpha)H^3$ and $O^{16}(H^3,n)F^{18}$. Small amounts of Li^6 in the presence of excess oxygen will give rise to F^{18} radioactivity proportional to the amount of Li^6 present. It is of some interest to determine the Li^6 content of certain reactor materials. In addition, the combination of a precise Li^6 determination and a precise determination of total lithium by chemical means may lead to a measurement of the isotopic composition of normal lithium as it occurs in nature. If the isotope ratio measurement is precise to 1%, it may be useful in studying natural isotope variations of lithium in geological materials.

Experimental

Two experiments have been carried out in which dilute aqueous solutions of $LiNO_3$ were irradiated with slow neutrons from the ORNL Graphite Reactor*, and the induced β^+ radioactivity of 1.87 hour F^{18} was measured with a well-type scintillation counter.

The results of experiment 1 are listed in Table I. Reagent grade Li_2CO_3 (of normal isotopic composition) was dissolved in concentrated nitric acid and diluted with distilled water to the lithium concentrations indicated. Solution volumes of 1.5 ml enclosed in polystyrene capsules were irradiated for 2 hours, and suitable aliquots were counted continuously during the period 2 to 9 hours after irradiation. Each decay curve was resolved into a long-lived tail (assumed to be 15 hr Na^{24})

*Slow neutron flux approximately 6×10^{11} $n/cm^2/sec$.

and a component of ca 1.8 hour half-life. From the resolved decay curves the net radioactivity of F^{18} was read at 4.5 hours after irradiation. The last column of Table I lists the amount of radioactivity observed in each sample per millimole of lithium present. The values are independent of lithium concentration although the most dilute solutions deviate. Samples 5 and 6 showed large amounts of radioactivity other than F^{18}, and decay curve analysis was difficult.

Table I

Experiment 1

Sample No.	Li^+ Conc. Moles/liter	Apparent $t_{1/2}$ (hr)	Net F^{18} Activity per millimole Li (10^6 c/m)
1	0.103	1.84	2.59
2	0.103	1.84	2.64
3	0.0103	1.75	2.72
4	0.0103	1.80	2.65
5	0.00103	1.65	4.08
6	0.00103	1.75	4.52

A γ-ray spectrum of sample 1, obtained by a γ scintillation spectrometer, showed a prominent γ photopeak at 0.51 Mev and very little other radioactivity. A similar γ-ray spectrum of sample 6 showed other higher energy γ radiations in addition to the 0.51 Mev maximum.

Experiment 2 was carried out similarly to experiment 1 with the exception that quartz-distilled water was used in preparing all solutions and polyethylene bottles were used in storing solutions until irradiation. Irradiation of 1.5 ml samples was for 3 hours, and counting was carried out during the period 2 to 9 hours after irradiation. In this experiment, samples containing pure water were included, and small amounts of radioactivity were induced in these which were resolved into 15 hour and ca 1.1

hour half-life components. For each sample, the water blank counting rate was subtracted from the total to obtain the net F^{18} radioactivity 3 hours after irradiation. These results are listed in Table II and plotted in Figure 1.(Sample 16 is anomalous.)

Table II

Experiment 2

Sample No.	Li^+ Conc. Moles/liter	Apparent $t_{1/2}$ (hr)	Net F^{18} Activity per millimole Li (10^6 c/m)
13	(H_2O blank)	--	--
14	(H_2O blank)	--	--
15	0.000663	1.67	6.16_5
16	0.000663	2.17	60.5
17	0.00398	1.92	4.80_2
18	0.00398		4.94_2
19	0.0239	1.83	5.32
20	0.0239	1.87	5.45
21	0.143	1.87	5.37_5
22	0.143		5.44_7
23	0.86	1.83	5.22
24	0.86		5.12
25	5.16	1.76	4.40
26	5.16		4.59

Examination of Figure 1 shows that aqueous lithium solutions more dilute than about 0.2 M give rise to F^{18} radioactivity in proportion to the lithium concentration. In very dilute solutions the results were somewhat erratic, but careful elimination of contaminating elements in the water and irradiation capsule may show the proportionality to be equally valid here. In concentrated solutions, the radioactivity per millimole of lithium is

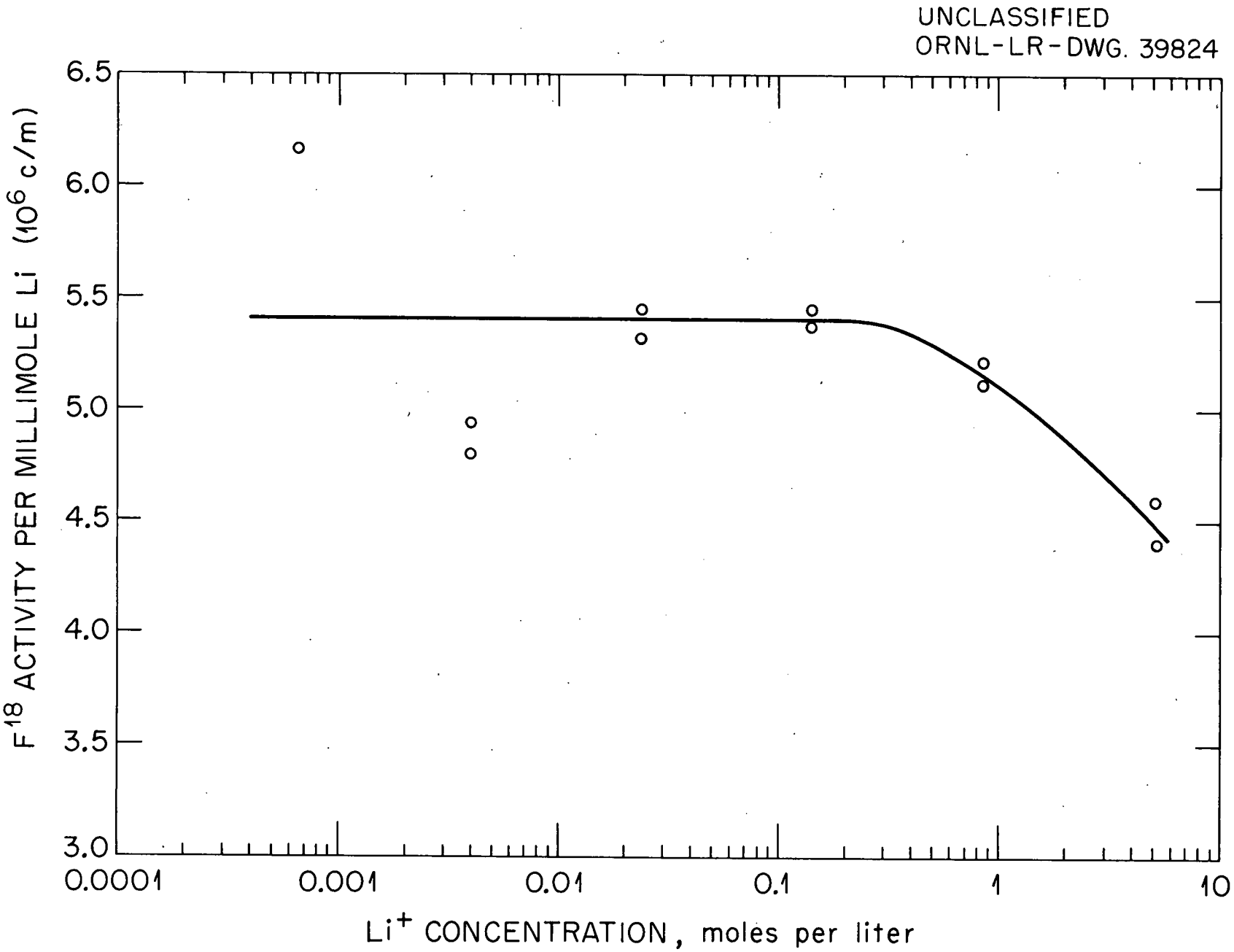

FIGURE 1

less, largely due to self-shielding of the neutron flux by the sample.*

Conclusions

These experiments demonstrate the feasibility of determining Li^6 in aqueous solutions by neutron activation and counting induced F^{18} radioactivity. The sensitivity is very high, 0.1 micromole of normal lithium being sufficient for 500 counts per minute of induced 1.87 hr F^{18} radioactivity.

*Taking as the total neutron absorption cross-section for normal lithium (7.5% Li^6) σ = 67 barns/atom or Σ = 0.040 cm^2/millimole, we calculate for small flux attenuations, attenuation = 4ML%, where M = molar lithium concentration and L = average linear path length in cm. for neutrons in the sample.

References

1. R. G. Osmond and A. A. Smales, Anal. Chim. Acta 10, 117 (1954).

2. A. A. Smales and R. K. Webster, Anal. Chim. Acta 18, 587 (1958).

3. G. W. Leddicotte and L. C. Bate, Paper 40, Pittsburgh Conf. on Anal. Chem. and Appl. Spectroscopy, March 3-7, 1958.

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