DETERMINATION OF LOW RATES OF PRECIPITATION OR DISSOLUTION OF NICKEL IN AQUEOUS ELECTROLYTES ACCORDING TO THE β-ISOTOPE OF Ni^{63}

Ya. B. Skuratnik, M. A. Dembrovskii, L. I. Krasinskaya, and A. P. Pchel'nikov

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A number of problems, for example, the investigation of the corrosion of nickel, the adsorption of organic substances, the composition of passivating films, the study of the hydrogenation of metals, etc. can be resolved successfully by the use of such low-energy β-isotopes as H^3, Ni^{63}, C^{14}, S^{35}, etc. Measurement of the radioactivity of these isotopes by a spectrometer with liquid scintillators involves difficulties due to the partial extinguishment of the scintillations by various ions (H^+, OH^-, Fe^{3+}, etc.) present in a sample of the solution [1, 2]. To eliminate this effect, the extinguishing ions must be removed from solution either by neutralization [1], which leads to dilution of the sample, or by redistillation of the solution [2], which is not always possible. We attempted to eliminate the indicated difficulties by the use of scintillation granules, used to record high-energy β-isotopes [3, 4].

To substantiate the possibility and advisability of the use of scintillation granules,* we obtained an expression for the effectiveness of the recording of soft β-isotopes (H^3 and Ni^{63}) as a function of the diameter of the granules. In the derivation we used the following data and assumptions:

I. The absorption of β-particles in the sample to be analyzed occurs according to an exponential law.

II. The β-particles reaching the granules have the original energy spectrum.

III. The conditions of light collection in the system of solutions and granules are the same as in the liquid scintillator.

Assuming that the boundary of the solution/scintillator system has semiinfinite geometry, i.e., the scintillator and solution are separated by an infinite plane, we calculated the average thickness of a layer of the solution $\bar{r}$, from which the β-particles reach the scintillator, and the thickness of the effectively measurable layer of solution Δr, the activity of which is equal to the number of β-particles (n) reaching the scintillator per unit time.

On the basis of the assumption I, the expression for n takes the form:

$$n = \int_0^{\infty} \int_0^{\frac{\pi}{2}} AS \cdot \frac{\sin\alpha}{2} \cdot e^{-\mu r/\cos\alpha} \, d\alpha dr, \qquad (1)$$

where A is the specific radioactivity of the solution; α is the angle of incidence of β-particles on the surface of the scintillator; r is the range of β-particles in solution; S is the area of the scintillator/solution boundary; μ is the coefficient of absorption of β-particles ($\mu = 0.693/\Delta_{1/2}$, where $\Delta_{1/2}$ is the half-thickness).

Using (1), we obtain expressions for Δr and $\bar{r}$:

$$\Delta r = 0.36\Delta_{1/2}, \qquad (2)$$

*The granules were prepared at the All-Union Scientific Research Institute of Single Cyrstals (Khar'kov) and comprise polystyrene with additions of PPO and POPOP.

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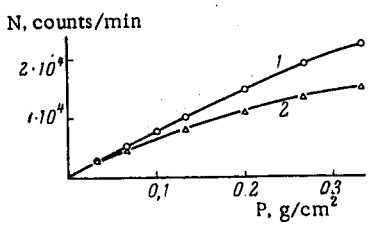

Fig. 1

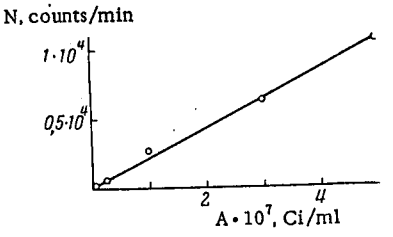

Fig. 2

Fig. 1. Dependence of the rate of count of a solution of Ni^{63} (1) with specific radioactivity $1 \cdot 10^{-7}$ Ci/ml and tritium (2) with specific radioactivity $2 \cdot 10^{-6}$ Ci/ml on the thickness P of scintillation granules in a weighing bottle with cross-sectional area 3 cm^2.

Fig. 2. Dependence of the rate of count on the specific radioactivity of a solution containing Ni^{63} and 100 ml of scintillation granules.

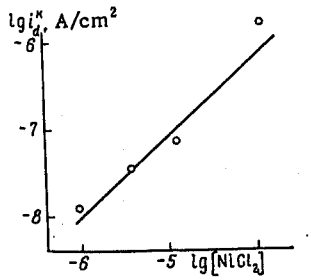

Fig. 3. Dependence of the rate of discharging of nickel on the $NiCl_2$ concentration at a potential of −0.54 V (normal hydrogen electrode) in a solution of NH_4Cl (2.97 M) + HCl (0.03 M).

$$\bar{r} = \frac{2}{3\mu} \approx \Delta_{1/2}. \tag{3}$$

Since the average diameter $\bar{d}$ of the granules used substantially exceeds $\Delta_{1/2}$ for the isotopes Ni^{63} and H^3, it follows from (3) that the conditions of semi-infinite geometry are realized for the solution–granule system. On the basis of this conclusion and the value for Δr, let us write the expression for the effectively measured fraction of the solution (ε_{geom}), representing the ratio of the amount of solution enclosed in the layer Δr to the entire amount of solution lying between the granules

$$\varepsilon_{geom} = \frac{2.16 \cdot \Delta_{1/2}}{(1/K - 1)\bar{d}}, \tag{4}$$

where K = 0.53 for $\bar{d}$ = 50 μ is the volume fraction of granules in the solution–granule system.

From (4) we obtain the following expression for the rate of count N (counts/min):

$$N = \varepsilon_{pl} AP \frac{2.16 \cdot \Delta_{1/2}}{\rho \bar{d}}, \tag{5}$$

where ε_{pl} is the effectiveness of recording of β-particles by the plastic scintillator; P is the weight of the granules, g. This expression cannot be verified directly, since the value of ε_{pl} is unknown. Therefore, we experimentally verified the ratio N/N_{liq}, where N_{liq} is the rate of count of a sample with volume V (ml) with specific activity A (Ci/ml) in a liquid scintillator. Let us write the expression for N_{liq} as follows:

$$N_{liq} = \varepsilon_{liq} VA, \tag{6}$$

where ε_{liq} is the efficiency of the recording of β-particles by a liquid scintillator of the ZhS-7 type.

Using (6) and the assumption that $\varepsilon_{pl} \approx \varepsilon_{liq}$, from (5) we obtain the expression:

$$\frac{N}{N_{liq}} = \frac{P \cdot 2.16 \cdot \Delta_{1/2}}{\rho V \bar{d}}. \tag{7}$$

The ratio of the experimentally obtained value of N/N_{liq} to that calculated according to formula (7) is 0.83 for Ni^{63} and 0.85 for H^3. This indicates the correctness of expressions (4) and (5).

*When smaller granules or β-isotopes of higher energy are used, the true geometry of the solution–granules system must be considered more accurately.

TABLE 1. Sensitivity of Recording in the Absence of the Effect of Quenching for a Liquid Scintillator (10 ml) and Scintillation Granules (2 g)

Isotope	Sensitivity of measurement, Ci/ml		Sensitivity of determination of elements, g/ml	
	liquid scintillator	scintillation granules	liquid scintillator	scintillation granules
H^3 (18 keV)	$5 \cdot 10^{-10}$	$5 \cdot 10^{-9}$	$2{,}5 \cdot 10^{-10}$	$2{,}5 \cdot 10^{-9}$
Ni^{63} (67 keV)	$2{,}5 \cdot 10^{-10}$	$1 \cdot 10^{-10}$	$6 \cdot 10^{-9}$	$2{,}5 \cdot 10^{-9}$
C^{14} (155 keV)	$2 \cdot 10^{-11}$	$0{,}7 \cdot 10^{-11}$	$4 \cdot 10^{-10}$	$0{,}5 \cdot 10^{-10}$
S^{35} (167 keV)	$2 \cdot 10^{-11}$	$0{,}7 \cdot 10^{-11}$	$2 \cdot 10^{-12}$	$0{,}7 \cdot 10^{-12}$

Thus, for granules with $\bar{d} = 50\ \mu$, $\varepsilon_{geom} = 0.25$ for Ni^{63} and $\varepsilon_{geom} = 0.03$ for H^3.

The dependence of N on the layer thickness of the granules P (g/cm^2) for Ni^{63} is linear all the way up to P = 0.3 g/cm^2 (Fig. 1). This permits the introduction of up to 2 g into industrial Teflon cuvettes, included in the USS-1 set, and up to 1.2 g of granules into glass weighing bottles, which are then inserted into the Teflon cuvettes. The background for 2 g of granules is ~ 150 counts/min at $\varepsilon_{pl} \approx 40\%$ for Ni^{63} and $\varepsilon_{pl} \approx 20\%$ for H^3. According to these data let us estimate the sensitivity of the recording of H^3 and Ni^{63} (see Table 1).

From Table 1 it is evident that the sensitivity of the recording of Ni^{63} by the granules is 2.5 times as high as by the liquid scintillator. The advantages of the granules were especially graphically revealed in a study of the influence of the composition of the electrolyte on the efficiency of recording. It was established that the efficiency of the recording of Ni^{63}, and, consequently, the sensitivity as well do not depend on the nature of the acid (HCl, H_2SO_4, HNO_3) and its concentration (0.01-5 M), nor on the presence of NaOH (0.1-6 N) and NH_4Cl (3 M) in the sample to be analyzed. The absence of time effects and the presence of a linear dependence of N on the specific activity of the sample (Fig. 2) are evidence of the absence of adsorption of Ni^{63} on the granules.

Since the operation of preliminary neutralization of the electrolyte is eliminated when granules are used, the sensitivity of the determination of nickel in acid and alkaline media is approximately an order of magnitude higher than when a liquid scintillator is used. Thus, in 6 N NaOH, when nickel with specific radioactivity 1.3 mCi/g is used under conditions analogous to [1], the use of granules permits a measurement of the corrosion rate $1 \cdot 10^{-7}$ A/cm^2.

The use of this method to study the cathodic deposition of nickel was demonstrated for the joint discharging of indium and nickel from chloride solutions on an indium cathode. For these purposes we used Ni with specific radioactivity 0.04 Ci/g.

The rate of deposition of nickel was calculated both according to the decrease in the radioactivity of the solution and according to the increase in the radioactivity of the electrode. In the latter case, an indium electrode, representing a galvanic deposit of indium on platinum, was entirely dissolved in the minimum volume of HNO_3 and the radioactivity of the solution obtained was measured. The rate of deposition of nickel at a potential lying in the region of the limiting current of the discharging of nickel is directly proportional to its content in solution (Fig. 3). As can be seen from the graph, the sensitivity of the determination of nickel permits a determination of the rate of its cathodic deposition around $1 \cdot 10^{-8}$ A/cm^2.

It should also be mentioned that the use of scintillation granules, which proved rather indifferent to various aggressive media, makes it possible to adjust the automatic continuous recording of the change in the radioactivity of the electrolyte with time, using low-energy β-isotopes as the label. For example, in an investigation of the anodic behavior of nickel labeled with Ni^{63}, the granules are introduced directly into the working volume of the cell, and optical contact of this cell with the photomultiplier of the USS-1 apparatus is ensured.

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