

ISOTOPIC EXCHANGE AND EVOLUTION OF METAL SURFACES
IN ELECTROLYTIC SOLUTIONS

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The exchange between atoms of a metal and its ions in aqueous solutions was first studied by von Hevesy¹ using $\text{ThB}(\text{Pb}_{212})$ as radioactive indicator in the system lead/lead nitrate. A striking aspect of the phenomena is that in a relatively short time hundreds of atomic layers of the metal are exchanged with the ions in solution. Since the diffusion of the tracer to the interior of the

metal is negligible at the temperatures at which these experiments were performed, von Hervey suggested that the very large amounts of exchange observed should be related to the heterogeneous structure of the metal surface.

More recently Haissinsky, Cottin and Varjabedian² investigated the exchange between various metals and their ions in solution. They found that for a given system the amount and rate of exchange depend on several factors such as the concentration of the solution, the temperature, the structure of the surface and on the anions present in the solution. These authors suggested that the reversible electron transfer $M^{+Z} + ze^{-} = M^0$ is very rapid and independent of the structure of the surface³. However, the metal surface does not remain unaltered at the contact with the electrolytic solution. In such conditions the exchange process disintegrates the original structure of the surface, leading to a recrystallization of atoms on it. The continuous renovation of the surface increases the number of atomic layers of the metal which exchange with the ions in solution.

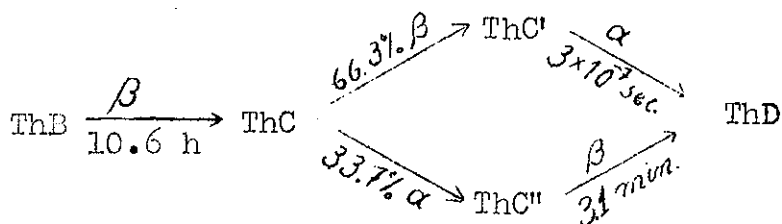
A necessary consequence of this proposed mechanism is that after a certain time of exchange has elapsed, a fraction of the radioelement used as tracer must be found in the interior of the metal, included in the recrystallized material. If so, accurate measurements should reveal a loss in the energy of the radiation emitted by the radioelement. When the tracer decays by α -particle emission, such loss of energy can be detected by measuring the range of the α -particles in nuclear emulsions.

Since the number of elements which have an α -emitting iso-

tope is very limited, the experiments could be performed only with a few metals. However, we found possible to extend these studies to a number of metals by a procedure which does not involve an isotope of the metal investigated.

EXPERIMENTAL AND RESULTS

The radioelement used in these experiments was $\text{ThC}(\text{Bi}_{212})$ in equilibrium with its parent ThB and derivatives. The decay of ThB is represented



It can be seen that ThB with its derivatives decay with 10.6 hours period and emit two main groups of α -particles, of 6.05 Mev from ThC (60.5 min period) and 8.776 Mev from ThC' (Po_{212} , 3×10^{-7} sec period). These radioelements were obtained from a thoron emanating radiothorium source and their activities were measured with a thin window G.M. counter.

All the experiments were done at room temperature $(25 \pm 3)^\circ \text{C}$ with mechanically polished metal surfaces with 1 cm^2 geometrical area, made from high purity metals. For all experiments, the time during which the foils were in contact with the solution was 30 minutes. The technique used for detecting the loss in energy of the α -particles was the usual autoradiographic method⁴ with

Ilford C-2 100 μ nuclear emulsions.

In a first series of experiments we investigate the exchange between a Bi foil and a 0.1 M $\text{Bi}(\text{NO}_3)_3$ solution with ThC as tracer, in 1 M HNO_3 media. The experimental conditions were similar to those described by Haissinsky². Relatively high activities of the tracer were used, in order to record a convenient number of tracks in the emulsion (approximately 10 per microscope field) in an exposure of some minutes. After being immersed during half hour in the solution, the Bi foil was thoroughly washed with water, dried and placed in contact during 10 minutes with the emulsion. After being developed the emulsion was scanned by means of a binocular Zeiss microscope with oil immersion objective (magnification \sim 1500 times). The range measurements have been limited to those particles that enter the emulsion through its upper surface and which have a maximum depth in the dry emulsion equal to or less than 1μ ⁵. Approximately 500 of such tracks were measured and the statistical distribution obtained is shown in figure 1.

Previous experiments with nuclear emulsions⁶ have shown that electrodeposits of ThC on several metals such as Au, Ag, Pb and Ni, obtained from hydrochloric and nitric acid media, do not exhibit penetration of the radioelements into the metals. For this reason a spontaneous deposit of ThC was prepared on a Ni foil, from a 0.5 M HCl solution. After being washed and dried, the foil was placed in contact with the emulsion. After development the measurements were made with the technique described above. The histogram obtained is shown in figure 2; it can be seen that it exi-

bits two sharp maxima at 27.5μ and 118.5μ . These values are in good agreement with those reported by other authors⁷ for ranges of ThC and ThC' α -particles in the emulsion.

It can be seen that histograms in figures 1 and 2 differ considerably. The distribution obtained from the Bi foil shows markedly greater dispersion of the track lengths and the modes of the distributions are found at shorter ranges than those obtained with the Ni foil (we shall hereafter refer to the histogram of figure 2 as the "standard distribution").

For quantitative comparison we have chosen to compute the mean track length of the distributions. This is a more precise and more sensitive procedure than the usual one of comparing the modes of the histograms, since in this last method no account is taken of the increase in dispersion. The calculations were carried out on the distribution from ThC' α -particles only, since the precision of the measurements of the smaller tracks due to the ThC is relatively poor. However, it can be seen that there is a region of the histogram where the distribution of ThC' tracks overlap with that of ThC. In calculating the average values the assumption was made that all tracks with range greater than 32μ originate from ThC' atoms.

A difference of 5.2μ was found between the mean track lengths of the standard distribution of ThC' tracks and the distribution obtained from the exchanged radioelement on the bismuth foil (table 1, column 5). This result shows that the α -particles emitted from the Bi foil possess, on the average, less energy than those detected in the standard conditions, indicating that an

appreciable fraction of the exchanged ThC atoms are not on the surface of the metal.

The experiments with other metals, such as Zn for example, were carried out by a different method, since this element does not have an α -emitting isotope. The electrical potential difference between a Zn foil and a 0.5 M ZnSO_4 solution (pH = 4) is approximately -0.52 volts, referred to the saturated calomel electrode ; if ThC is added to the solution, the radioactive atoms will be spontaneously deposited on the Zn foil⁸. In this system two process will occur simultaneously : the exchange $\text{Zn}^{+2} + 2e^- = \text{Zn}^0$ and the deposition of ThC on Zn. If the metal surface is altered in consequence of the exchange process, the ThC deposits on a surface which is undergoing evolution and recrystallization . This could be revealed, as previously, by measuring the ranges of the α -particles in the emulsion. The distribution of α -tracks obtained in such an experiment is shown in figure 3. The mean track length of the ThC' α -particles calculated from this distribution is 41.7μ , indicating that a part of the radioelement is inside the metal foil.

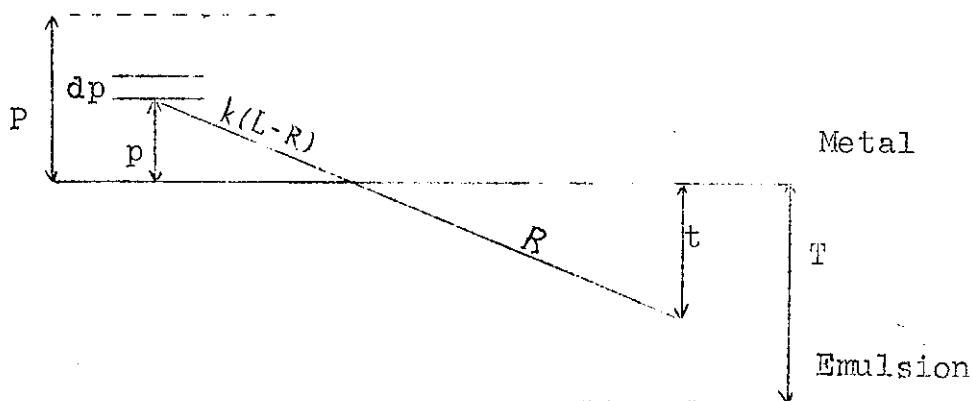
Marked alterations in the distribution of the α -particles were observed with deposits of ThC on Pb and Cd (figures 4 and 5). For these metals, as for Zn, the autoradiography showed that the distribution of the radioelement on the metal was not uniform, since a part of the α -tracks were found concentrated at small areas of the nuclear plate. A similar result was observed . by Simnad¹⁰ for other metals in autoradiographic studies with X-rays films.

The results obtained with Cu, Ni and Mn are shown in figures 6, 7 and 8 ; it can be seen that these histograms do not differ considerably from the standard distribution. However, the calculated mean track lengths of the α -particles is shorter than that obtained in standard conditions (table 1, column 2).

The reproducibility of the results using different foils from the same metal was investigated for some systems and differences $\leq 1\mu$ in the mean track length of the α -particles were observed. With Cd however larger differences were obtained ($\leq 1.6\mu$).

DISCUSSION

In order to interpret the above results we calculated the mean range \bar{R} of the α -particles in the emulsion to be expected with the measurement technique we have used, assuming that the radioelement is distributed in the metal with a density $\delta(p)$, which is a function of the depth p of penetration in the metal.



The number of α -particles $N(\theta)d\theta$ emitted at an angle be-

tween θ and $\theta + d\theta$ is proportional to $\cos\theta$. It can be seen from figure 9 that $\sin\theta = \frac{p}{k(L - R)}$, where L is the range of the α -particles emitted from the radioactive atoms at the surface of the metal and k the ratio of the stopping power of the emulsion to that of the metal. Thus, the distribution in range $N(R, p)$ to be expected from that part of the radioelement that is localized at a depth p is

$$N(R, p)dp = \frac{p}{k(L - R)^2} dR \quad (1)$$

It can easily be seen that tracks of a given range R that are accepted for measurements (depth in the emulsion \leq maximum depth T) must have their origins at depths $p \leq p'$, where

$$p' = \frac{kT(L - R)}{R} \quad (2)$$

The average range \bar{R} of all tracks with range greater than BL is thus given by

$$\bar{R} = \frac{\int_{BL}^L \int_0^{p'} N(R, p) \delta(p) dp dR}{\int_{BL}^L \int_0^{p'} N(R, p) \delta(p) dp dR} \quad (3)$$

In our computations we chose $BL = 32\mu$ in order not to include any ThC α -particles.

Now, if we assume that $\delta(p) = 1$ for p between 0 and a given value P_{\max} and $\delta(p) = 0$ for $p > P_{\max}$, that is, a uniform distribution of radioelement in a layer of thickness P_{\max} and no radioelement at depths greater than P_{\max} , the integrals

in (3) reduces to :

$$\bar{R} = \left[\int_{BL}^P \int_0^R \frac{\frac{LkT}{P+kT}}{k(L-R)^2} pdpdR + \int_{\frac{LkT}{P+kT}}^L \int_0^R \frac{kT \frac{L-R}{R}}{k(L-R)^2} pdpdR \right] \times$$

$$\times \left[\int_{BL}^P \int_0^R \frac{\frac{LkT}{P+kT}}{k(L-R)^2} pdpdR + \int_{\frac{LkT}{P+kT}}^L \int_0^R \frac{kT \frac{L-R}{R}}{k(L-R)^2} pdpdR \right]^{-1} \quad (4)$$

Performing the integration one obtains :

$$\bar{R} = \frac{L}{2} \left[1 - A \ln \frac{(1+A)(1-B)}{A} + \frac{1}{A} \ln(1+A) - \frac{AB}{1-B} \right] \frac{1}{1 - \frac{AB}{2(1-B)}}$$

where $A = P_{\max} / kT$

In figure 9 we have plotted $\frac{L-\bar{R}}{R}$, the relative shortening as a function of $1/A$. Taking L as the mean range of the standard distribution we calculated the relative shortening for the various systems studied (table 1, column 6) and from the graph we obtained the corresponding $1/A$ values (column 7). T was equal to 2.4μ in all the measurements; the value of k for the various metals was calculated from the data compiled by Mano¹¹ (column 8). The values of the maximum depth $P_{\max} = kTA$ are listed in column 9. The number of atomic layers corresponding to a

depth P_{\max} was calculated assuming a close-packed structure of spherical atoms¹² and the values obtained are listed in column 10.

The contribution of the diffusion of the tracer into the metal to the value of P_{\max} is negligible. When a uniform thin layer of tracer is allowed to diffuse into an infinitely thick media, the concentration of the tracer at a distance between x and $x+dx$ from the surface at a time t is given by¹³

$$C = \frac{C_0}{\sqrt{\pi D t}} e^{-x^2/4Dt} \quad (5)$$

where C_0 is the concentration at $t = 0$ and $x = 0$. For diffusion of ThC in Pb for example, D at 25°C ¹⁴ is approximately $3 \times 10^{-16} \text{ cm}^2 \text{ x sec}^{-1}$, $x = P_{\max} = 0.206 \mu$ and $t \sim 30$ minutes; with these values the relation (5) gives¹⁵

$$\frac{C}{C_0} < 10^{-60}$$

The depth of penetration P_{\max} is intimately connected with the alterations of the metallic surface in consequence of the exchange process. The comparison between the values of P_{\max} for the various systems studied (neglecting in a first approximation the specific influence of the anion), indicates that the alterations on the surfaces of Zn, Bi, Pb and Cd were more intense than that on Cu, Ni and Mn. The same conclusion was derived by Haissinsky^{2,3} from exchange experiments, who observed that this is in agreement with the classification proposed by Piontelli¹⁷ relating the electrochemical properties of metals with their crystal

and electronic structure. According to these ideas the small tendency of the transition metals to exchange with the ions in the solution is a consequence of their high cohesion in the lattice, due to the participation of d orbitals in the bonding between the atoms (hybridization s, p, d):

The values of P_{\max} obtained must be considered only as semi-quantitative in view of the extreme simplicity of the geometrical model we proposed. However, a simple comparison with data from exchange experiments (column 11) shows that for Bi and Pb the values of P_{\max} and the number of exchanged layers are of the same order of magnitude. For Cu the depth of penetration calculated is much smaller than that to be expected from the exchange experiments. On the basis of our assumptions this would mean that the distribution of the radioelement $\delta(p)$ is highly non-uniform, with increasing density near the metal surface. It seems possible to derive the distribution of density $\delta(p)$ of the radioelement in the metal, from experiments realized in "good geometry" instead of the autoradiographic technique. Although it is clear that $\delta(p)$ does not represent the true distribution of the radioelement in the metal, it may nevertheless be helpful in correlating the behaviour between the surfaces of various metals in electrochemical studies, corrosion investigation, etc..

1. von Hevesy - Phys. Z. 16, 52 (1915)
2. M. Haissinsky, M. Cecchin et B. Varjabedian - J. Chim. Phys. 45, 212 (1948)
3. M. Haissinsky - Iden, 45, 224 (1948)
4. H. Yagoda - "Radioactive Measurements with Nuclear Emulsions" - John Wiley and Sons, N. Y. (1949)
5. This corresponds to a maximum depth of approximately 2.4μ in the unprocessed emulsion⁷.
6. J. Danon et M. Haissinsky - J. Chim. Phys. 49, C 123 (1952)
7. A. Beiser - Rev. Mod. Phys. 24, 273 (1952)
8. The solutions used in our experiments were approximately 10^{-14} M in ThC ions to which corresponds a critical deposition potential of about -0.30 volts, assuming the validity of the Nernst law (see reference 9)
9. M. Haissinsky - Experientia, 8, 125 (1952)
10. M. T. Simnad - "Properties of Metallic Surfaces" - Monograph 13, pg. 23 Institute of Metals, London (1952)
11. G. Mano - Ann. Phys. 1, 407 (1934)
12. R. C. Evans - "Crystal Chemistry", pg. 94, Cambridge U.P. (1952)
13. J. H. Wang - "Radioactivity Applied to Chemistry" pg. 62, John Wiley and Sons, N. Y. (1951)
14. R. Eyrer - "Diffusion in and through Solids" pg. 275, Cambridge U. P. (1941)
15. This does not include the possible influence of lateral diffusion; for a relevant discussion see reference 16.
16. C. V. King - Ann. N. Y. Acad. Sc. 53, 918 (1953)
17. R. Piontelli - J. Chim. Phys. 45, 115 (1948); C. h. Comm. Int. Therm. Cin. Electrochim. 2, 149, 163 (1950)

TABLE 1

system	\bar{R}_{ThC}	\bar{R}_{ThC}	C_{ThC}	N	Δ	$\frac{\Delta}{L^x}$ $\times 10^2$	1/A	k	P	P_1	E_i
standard Ni 0.5 M HCl	26.7	47.7	3.4	371	-	-	-	-	-	-	-
Bi/Bi ⁺³ 0.1 M Bi 1 M HNO ₃	20.7	42.5	4.3	321	5.2	10.9	7.9	0.67	2.030	~850	~1000
Zn/Zn ⁺² 0.5 M ZnSO ₄ pH=4.2	22.1	41.7	4.1	274	6.0	12.6	5.8	0.49	2.020	~950	
Pb/Pb ⁺² 0.1 M Pb(CH ₃ COO) ₂ pH = 5.0	21.0	42.5	5.1	318	5.2	10.9	7.9	0.56	1.700	~600	~1000
Cd/Cd ⁺² 0.5 M CdSO ₄ pH = 4.7	23.6	42.9	5.5	192	4.8	10.0	9.5	0.53	1.350	~550	
Cu/Cu ⁺² 0.3 M CuBr ₂ pH = 3.4	25.0	43.7	4.5	459	4.0	8.4	12.8	0.39	740	~350	~11,000
Ni/Ni ⁺² 0.5 M NiCl ₂ pH = 4.8	25.1	45.5	4.8	323	2.2	4.61	31	0.37	290	~140	
Mn/Mn ⁺² 0.5 M MnSO ₄ pH = 4.1	25.9	46.5	3.8	283	1.2	2.52	65	0.46	170	~80	

- \bar{R}_{ThC} - mean range of ThC α -particles in the emulsion
- \bar{R}'_{ThC} - mean range of ThC' α -particles in the emulsion
- σ_{ThC} - standard deviation of the ThC' α -particles distribution
- N - number of ThC' α -tracks measured
- Δ - difference between the mean range of the ThC' tracks in standard distribution and in other distributions
- k - ratio of the stopping power of the emulsion to that of the metal
- P - maximum depth of penetration in the metal in angstroms
- P_1 - maximum depth of penetration in the metal in atomic layers
- E_1 - number of atomic layers of metal exchanged with the ions in solution (data from reference 2)

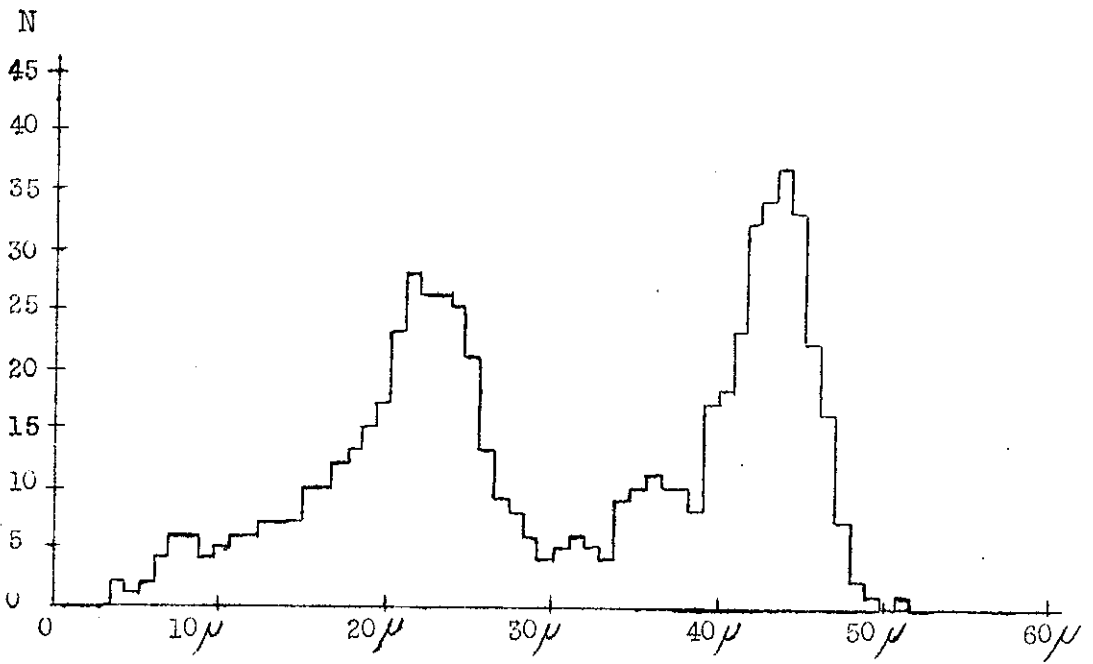


Figure 1. Bi

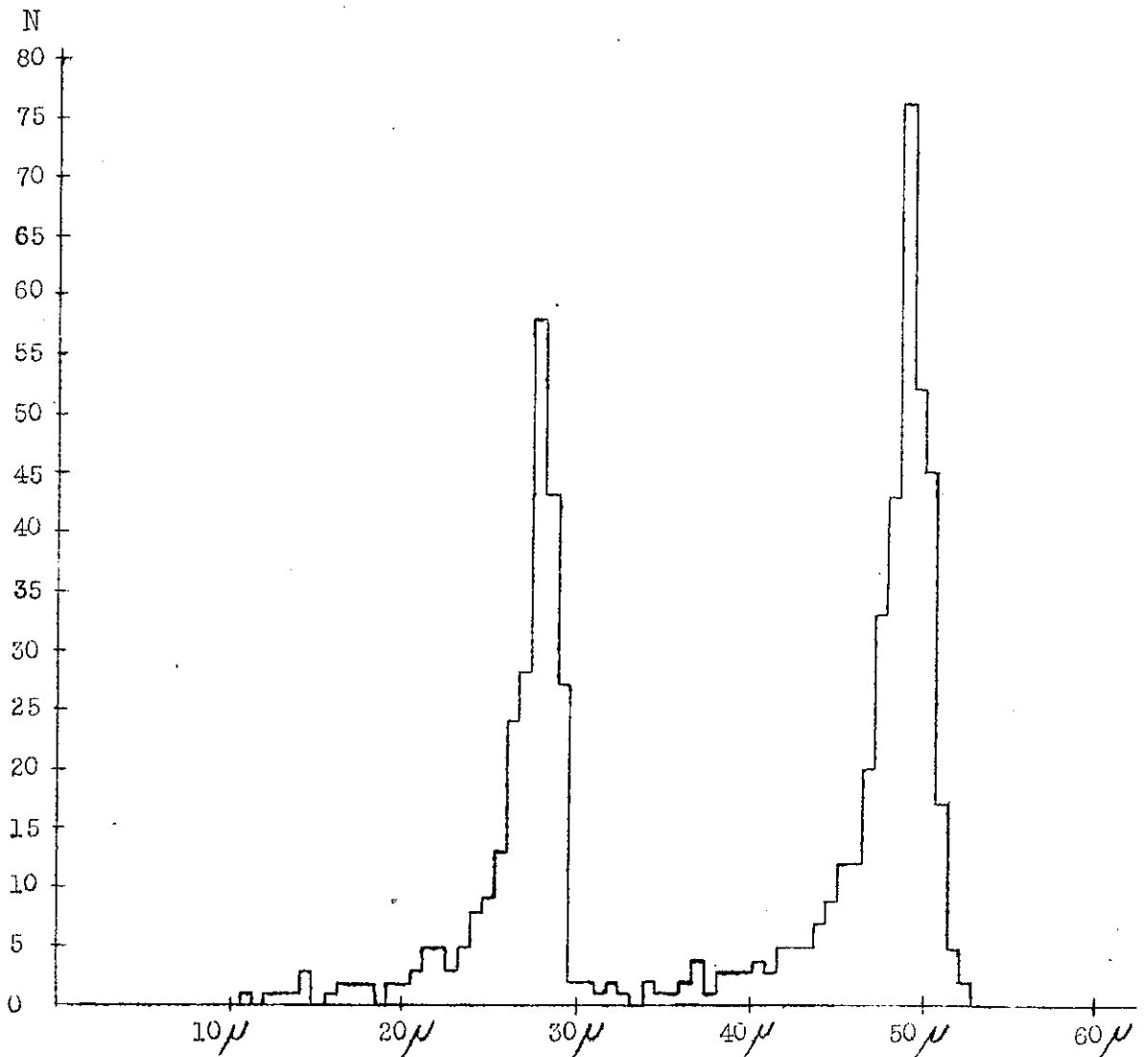


Figure 2 - "Standard distribution"- Ni

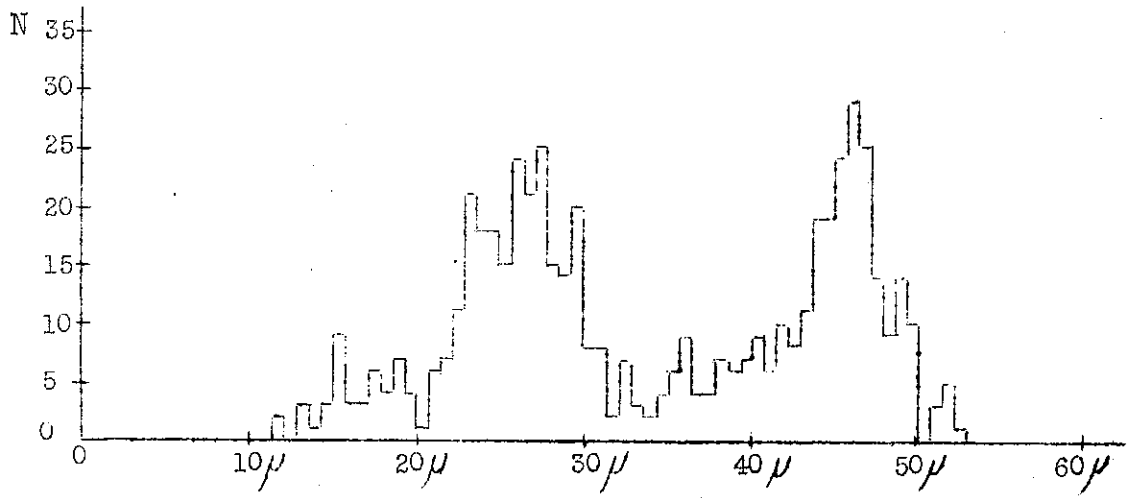


Figure 3 - Zn

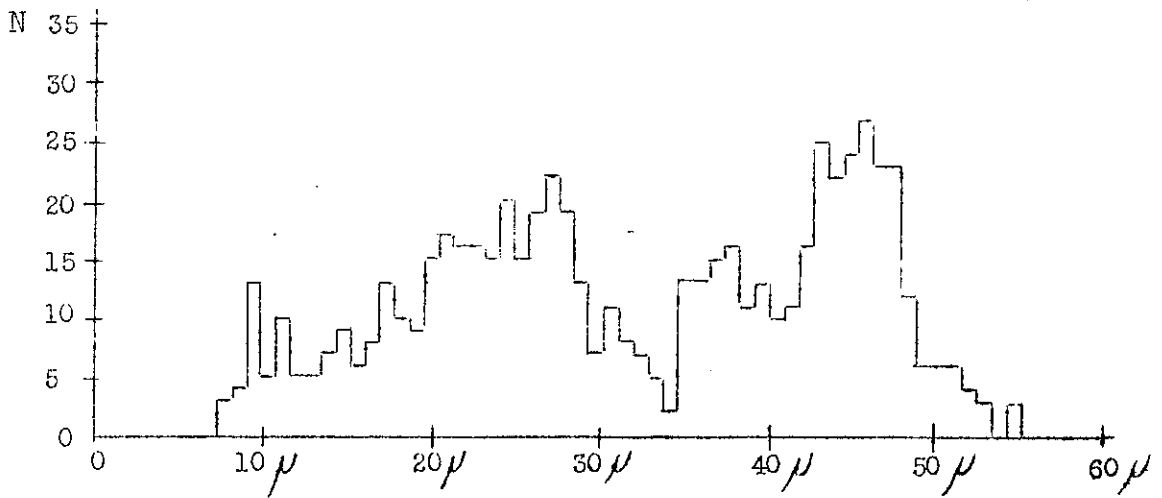


Figure 4 - Pb

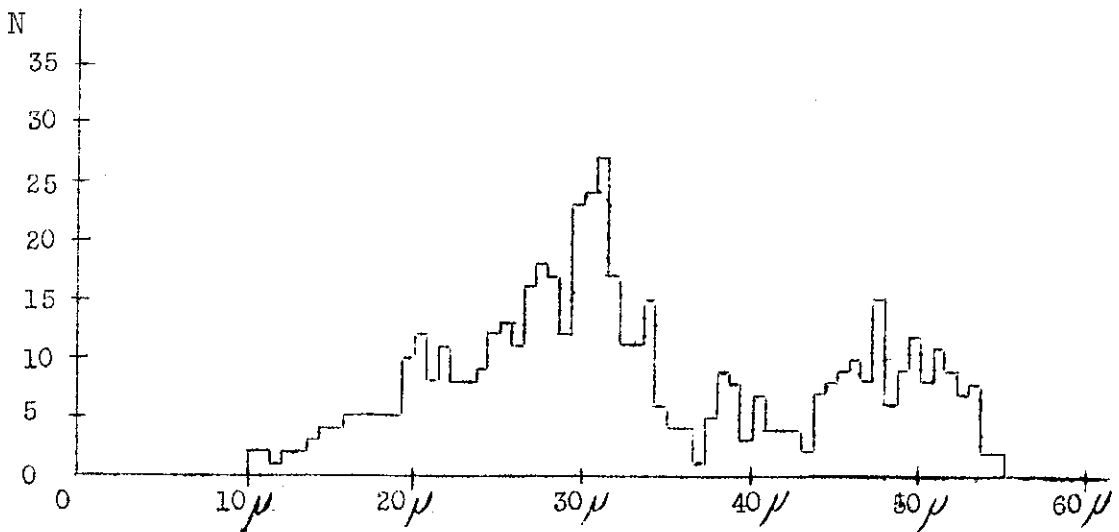


Figure 5 - Cd

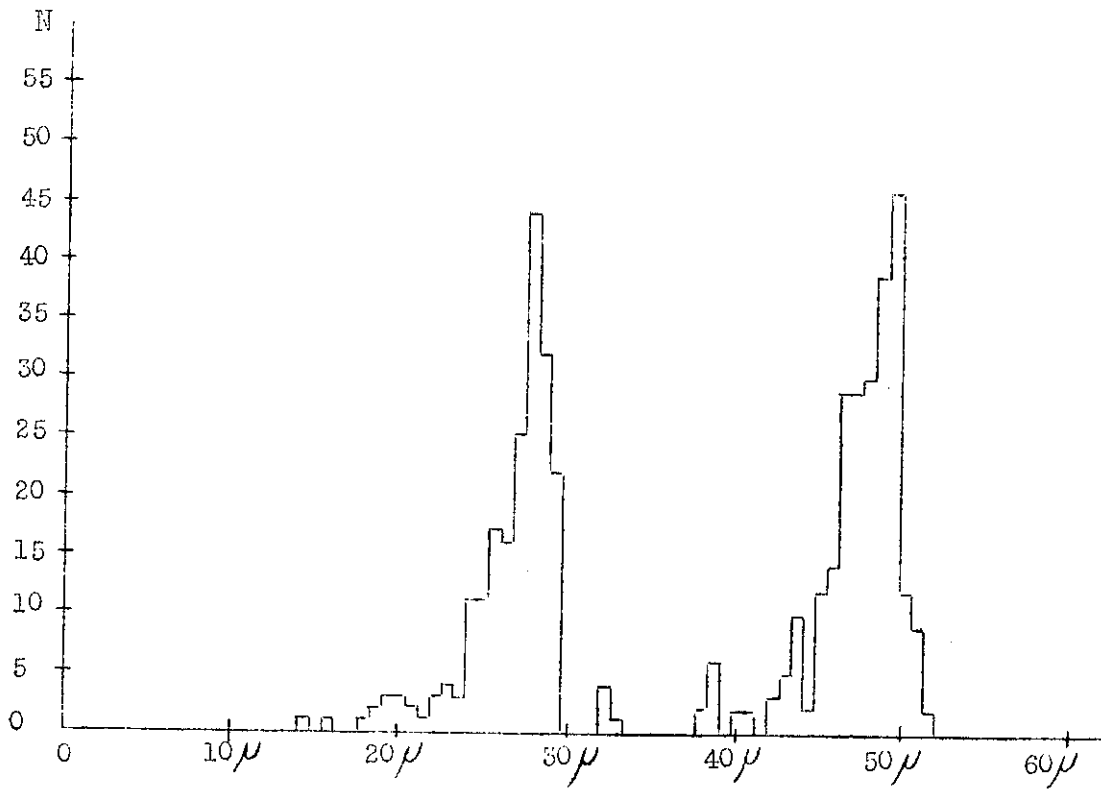


Figure 8 - Mn

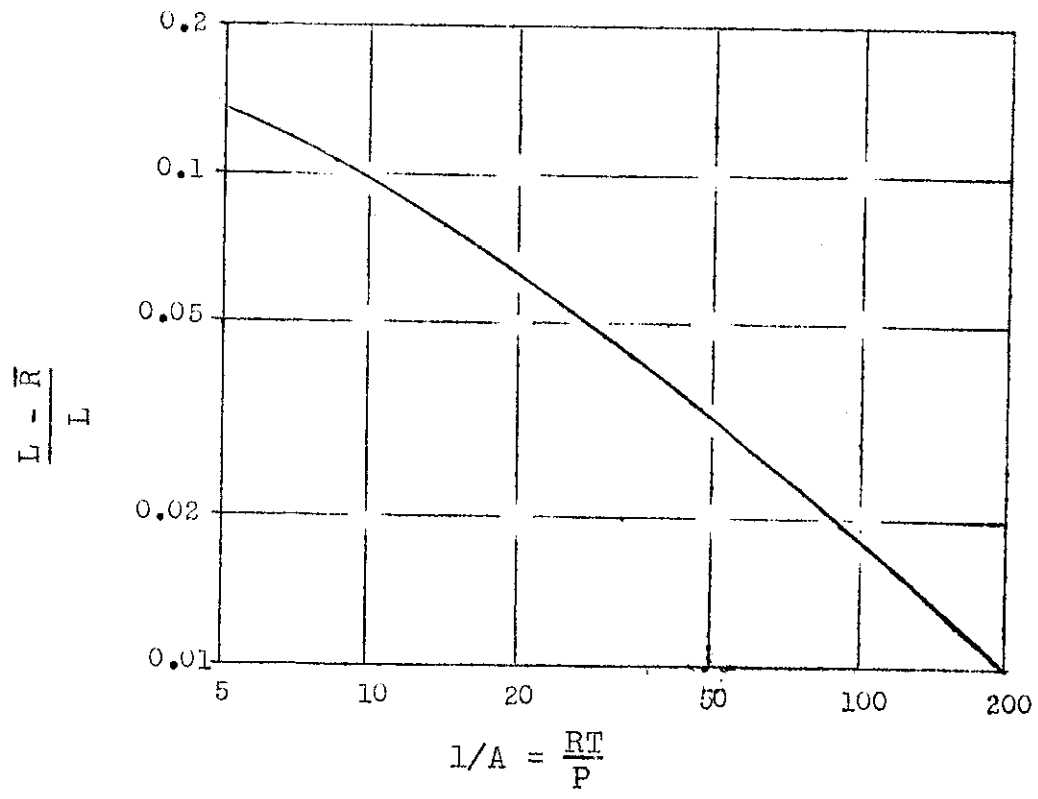


Figure 9

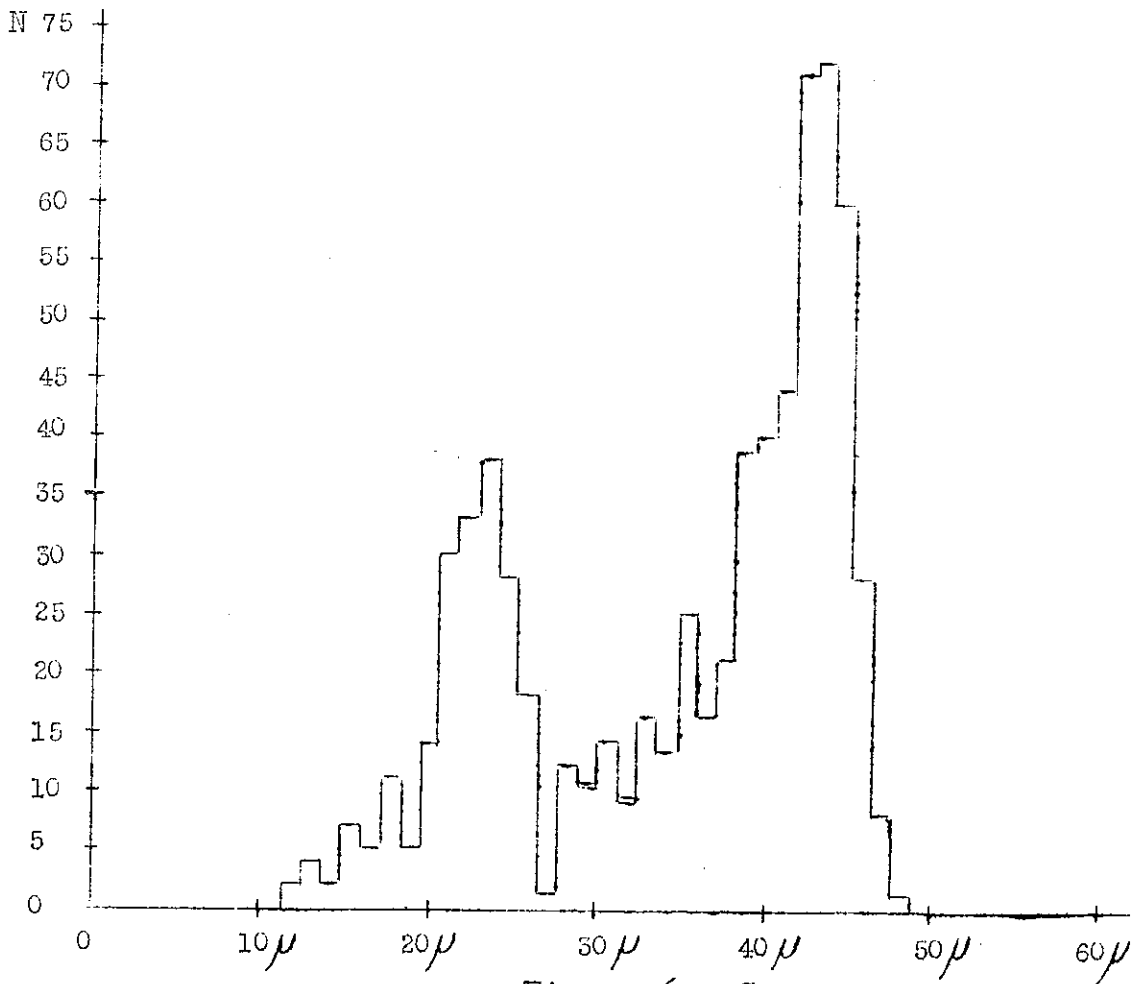


Figure 6 - Cu

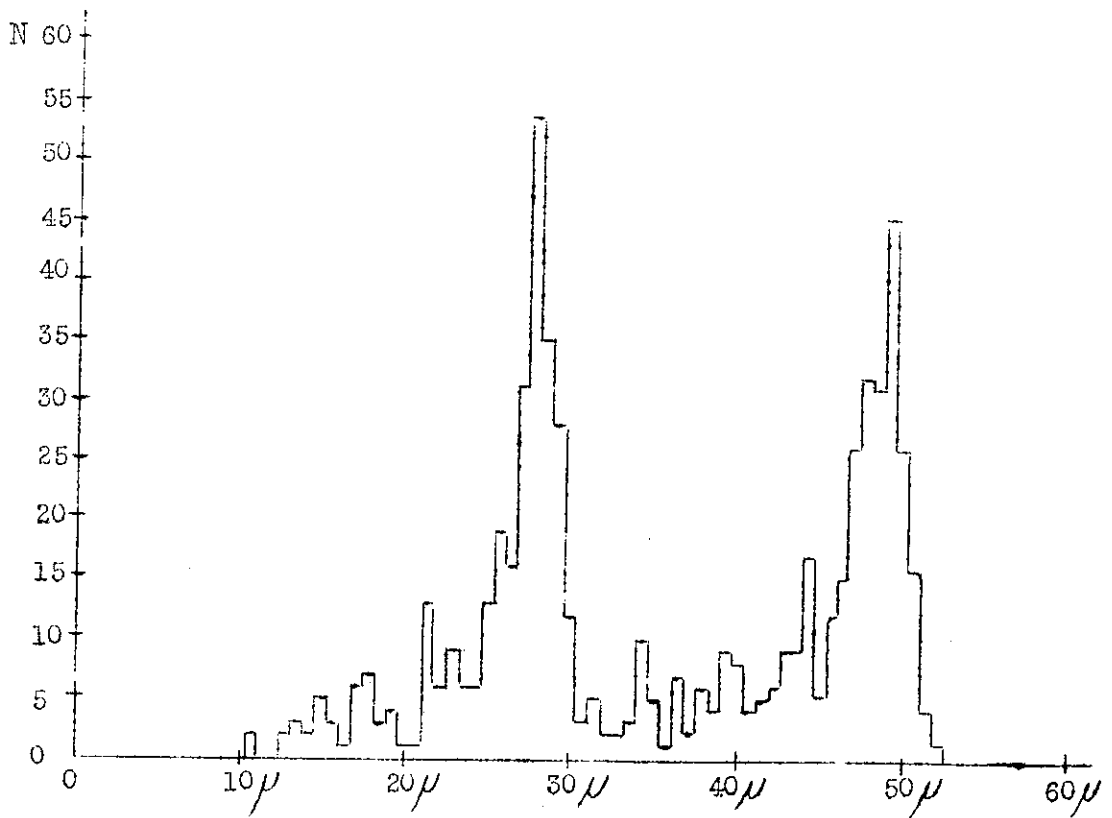


Figure 7 - Ni