EUR 458.e

REPRINT

EUROPEAN ATOMIC ENERGY COMMUNITY - EURATOM

FURTHER STUDIES ON RADIOCOLLOIDS

by

J.O. LILJENZIN, R. LINDNER and H. REINHARDT

1964

Joint Nuclear Research Centre
Ispra Establishment (Italy)
Chemistry Department

Reprinted from
RADIOCHIMICA ACTA
Vol. 1 - No. 4 - 1963

LEGAL NOTICE

EUR 458.e
REPRINT

FURTHER STUDIES ON RADIOCOLLOIDS by J.C. LILJENZIN, R. LINDNER and H. REINHARDT.

EUROPEAN ATOMIC ENERGY COMMUNITY - EURATOM
Joint Nuclear Research Centre - Ispra Establishment (Italy)
Chemistry Department
Reprinted from "RADIOCHIMICA ACTA" Vol. 1 - No. 4-1963, pages 199-203.

The continuous measurement of the diffusion of radiocolloids is made possible by use of a photomultiplier tube viewing a ZnS-covered and thin walled glass capillary inside which the α-radiating particles diffuse in aqueous suspension and get adsorbed at the surface.

The method was shown to yield satisfactory results for the particle size of alumina powder of known grain size distribution tagged with (Pb+Bi)-212 or Po-210.

Po-210 radiocolloids were found to have an average radius of about 10^{-4} cm and a "specific" radioactivity of about 10^{-4} whereas the values for radioactive particles generated by decay of Rn-220 in very pure water were 10^{-6} cm and about 10^{-4}. This means that "pure" (carrierfree) radiocolloids could not be shown to exist.

EUR 458.e
REPRINT

FURTHER STUDIES ON RADIOCOLLOIDS by J.C. LILJENZIN, R. LINDNER and H. REINHARDT.

EUROPEAN ATOMIC ENERGY COMMUNITY - EURATOM
Joint Nuclear Research Centre - Ispra Establishment (Italy)
Chemistry Department
Reprinted from "RADIOCHIMICA ACTA" Vol. 1 - No. 4-1963, pages 199-203.

The continuous measurement of the diffusion of radiocolloids is made possible by use of a photomultiplier tube viewing a ZnS-covered and thin walled glass capillary inside which the α-radiating particles diffuse in aqueous suspension and get adsorbed at the surface.

The method was shown to yield satisfactory results for the particle size of alumina powder of known grain size distribution tagged with (Pb+Bi)-212 or Po-210.

Po-210 radiocolloids were found to have an average radius of about 10^{-4} cm and a "specific" radioactivity of about 10^{-4} whereas the values for radioactive particles generated by decay of Rn-220 in very pure water were 10^{-6} cm and about 10^{-4}. This means that "pure" (carrierfree) radiocolloids could not be shown to exist.

Sonderdruck aus Radiochimica Acta 1, 199–203 (1963)

Further Studies on Radiocolloids

By H. REINHARDT, J. O. LILJENZIN, and R. LINDNER, Chemistry Department, CCR Euratom Ispra (Italy)

With 6 figures. (Received February 14, 1963)

Summary

The continuous measurement of the diffusion of radiocolloids is made possible by use of a photomultiplier tube viewing a ZnS-covered and thin walled glass capillary inside which the α-radiating particles diffuse in aqueous suspension and get adsorbed at the surface.
The method was shown to yield satisfactory results for the particle size of alumina powder of known grain size distribution tagged with (Pb+Bi)-212 or Po-210.
Po-210 radiocolloids were found to have an average radius of about 10^{-4} cm and a "specific" radioactivity of about 10^{-4} whereas the values for radioactive particles generated by decay of Rn-220 in very pure water were 10^{-6} cm and about 10^{-4}. This means that "pure" (carrierfree) radiocolloids could not be shown to exist.

Zusammenfassung

Radiokolloide gelangen durch Diffusion in wässriger Lösung an die Innenwand einer dünnwandigen Glaskapillare und werden dort adsorbiert.
Die von ihnen ausgesandte α-Strahlung erregt einen ZnS-Belag auf der Außenwand der Kapillare. So kann die Anzahl der diffundierten Kolloidteilchen mittels Fotovervielfacher laufend gemessen werden.
Die Methode ergab zufriedenstellende Ergebnisse bei der Berechnung der Korngröße (aus der Diffusionskonstante) von Al_2O_3-Staub indiziert mit (Pb+Bi)-212 oder Po-210.
Po-210 Radiokolloide zeigten eine durchschnittliche Teilchengröße von etwa 10^{-4} cm und eine spezifische Radioaktivität von etwa 10^{-4}. Für Radiokolloide, die nach Absorption von Thoron in hochgereinigtem Wasser vorgefunden wurden, waren die Werte ca. 10^{-6} cm bzw. ca. 10^{-4}. „Reine" (trägerfreie) Radiokolloide konnten also nicht festgestellt werden.

Résumé

La diffusion des radiocolloïdes est mesurée continuellement par un photomultiplicateur en contact optique avec un capillaire (couvert avec ZnS) dans lequel les particules rayonnants α diffusent et sont adsorbées à la surface intérieure.
La méthode a été calibrée avec des grains de Al_2O_3 qui avaient adsorbé (Pb + Bi)-212 ou Po-210.
Les radiocolloïdes de Po-210 ont été trouvés avoir un diamètre d'environ 10^{-4} cm et une activité spécifique d'environ 10^{-4}. Les particules radioactives trouvées dans l'eau extrêmement pure après absorption de Rn-220 sont d'un diamétre d'environ 10^{-6} cm et d'activité spécifique d'environ 10^{-4}. Ceci veut dire que nous n'avons pas pu montrer l'existence des radiocolloïdes proprement dits «purs» et sans entraineur.

Introduction

Radioactive species, especially those forming hydrolyzing ions have been shown long ago[1, 2] to occur in aqueous solutions as particles of colloidal size. The nature of these „radiocolloids" has been disputed: either
pure radioactive substances insoluble below concentrations belonging to their conventional solubility product – measured with macro amounts – or
adsorption compounds on insoluble foreign matter – e.g. dust – have been assumed.
Some years ago we started experiments in order to settle the question by quantitative measurements of the specific radioactivity – defined as the ratio of the actual radioactivity/mass ratio to that of the respective pure radioactive compound – of single radiocolloidal particles. This value is equal to one for "pure" radiocolloids and less than one for carrier radiocolloids. It can be found by determination of the mass through volume by measurements of diffusion[3] and sedimentation[4] and by determination of the radioactivity by evaluation of the tracks produced in a nuclear emulsion in contact with the particles.
This technique is used preferably for α-emitting isotopes. The first results, obtained mostly with Po-210, showed comparatively large particles (up to 1 micron). The size determination of such particles necessitates methods to measure diffusion constants as low as 10^{-9} cm^2 sec^{-1}. This can be done using "radial" diffusion in a glass capillary and the fact that the particles get adsorbed at the wall. From the time function of this process the diffusion coefficient can be calculated.

Theory

Fick's equation is for the present case (radial transport in a cylinder):

$$\frac{\partial c}{\partial t} = \frac{1}{r}\frac{\partial}{\partial r}\left(r D \frac{\partial c}{\partial r}\right). \qquad (1)$$

In our case the following boundary conditions are assumed to be valid (r is the radial distance from the centre of the capillary of radius a, c_0 the initial concentration):

$$\text{for } t = 0 \text{ and } 0 < r < a: \quad c = c_0 \qquad (2a)$$

$$\text{for } t \geqslant 0 \text{ and } r = 0: \quad \frac{\partial c}{\partial r} = 0 \qquad (2b)$$

$$\text{for } t \geqslant 0 \text{ and } r = a: \quad c = 0 \qquad (2c)$$

The solution of (1) for the case (2) is found[5] to be:

$$c(r, t) = \frac{2 c_0}{a} \sum_{n=1}^{\infty} e^{-D \alpha_n^2 t} \frac{J_0(r, \alpha_n)}{J_1(a, \alpha_n)} \qquad (3)$$

with $a\,\alpha_n$ being the positive roots of

$$J_0(a\,\alpha_n) = 0\,.$$

$J(x)$ is the Bessel function of the first kind of order zero.
The relative – non adsorbed – amount in the volume as function of time is given by:

$$\frac{I_t}{I_0} = \sum_{n=1}^{\infty} \frac{4}{a^2 \alpha_n^2} e^{-D \alpha_n^2 t} \qquad (4)$$

alternatively the adsorption time function can be written:

$$1 - \frac{I_t}{I_0} = \frac{4}{\sqrt{\pi}} \sqrt{\frac{Dt}{a^2}} - \frac{Dt}{a^2} - \frac{1}{3\sqrt{\pi}} \left(\frac{Dt}{a^2}\right)^{3/2} + \cdots \qquad (5)$$

(up to $Dt/a^2 \sim 0{,}16$ or $1 - It/I_0 \sim 75\%$ the contribution of the third term is less than 1% of the whole value). This function is reproduced in Fig. 1.

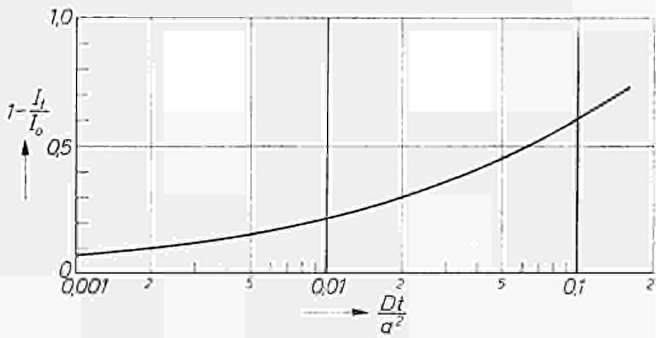

Fig. 1. Time function for diffusion in a capillary

Methods

Experiments using Eq. (4) are simple: the capillary is emptied after a certain time and the radioactivity in solution is measured[3].
It is, however, tempting to evaluate Eq. (5) continuously in one experiment in order to check the time function of diffusion and indirectly also particle size distribution and its eventual change in time. This latter point shall be treated in future investigations.
For that purpose radioisotopes with short range radiation, preferably α-radiation have to be used. The principle of the experiment is shown in Fig. 2.

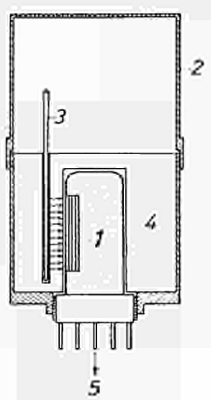

Fig. 2. Apparatus for continuous measurement of slow diffusion of α-radiating particles in solution

[1] F. Paneth, Über kolloide Lösungen radioaktiver Substanzen, Kolloid-Z. **13**, 297 (1913).
[2] cf. also G. K. Schweitzer and M. Jackson, Radiocolloids, J. Chem. Educat. **2**, 513 (1952).
[3] R. Lindner, H. Reinhardt und J. O. Liljenzin, Bestimmung der Größe von Poloniumradiokolloidteilchen, Z. Naturforsch. **15a**, 643 (1960).
[4] R. Lindner, J. O. Liljenzin und H. Reinhardt, Radiometrische Sedimentationsanalyse, Z. Naturforsch. **15a**, 1110 (1960).
[5] J. Crank, The Mathematics of Diffusion, p. 66, Oxford 1956.

A very thin-walled (10–20 μ) glass capillary (3) of about 2 mm diameter, produced by a special technique[6], is inserted into a plexiglas block (4), filled with the solution and shielded with a lighttight top (2) screwed on the lower half of the apparatus. The capillary has been covered with a thin ZnS layer by dipping the capillary in a suspension of ZnS in "Zapon lacquer" diluted with acetone and drying in air. Colloidal particles, containing the α-emitter and adsorbed on the innerwall, are registered by the ZnS-screen and the fotomultiplier. The function: activity registered (background subtracted) versus the logarithm of time follows in the case of uniform particle size the curve of Fig. 1. Thus Dt/a^2 and D can be evaluated.

In order to obtain a very pure diffusion medium part of the experiments were performed in the following way (cf. Fig. 3):

With a filtered stream of nitrogen (8), Rn-220 emanating from a 5 mC Th-228 (Ra-224) – source (6) is carried to and absorbed in water freshly distilled from quartz vessels into the very carefully cleaned apparatus. The whole apparatus is kept in a glove box. The water is kept above the diffusion capillary (3) by the gas pressure during the absorption period ranging from 5 to 200 minutes.

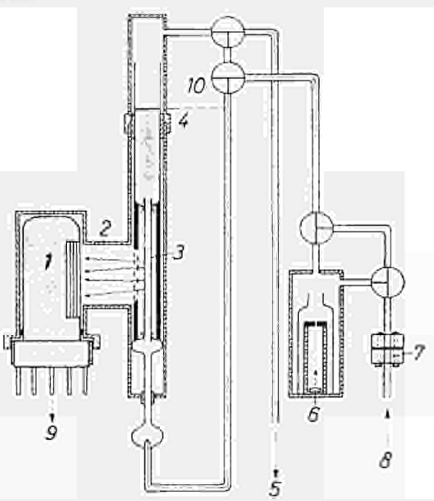

Fig. 3. Diffusion measurement on radiocolloids produced by absorption of emanation

By turning off the stopcock (10) the solution is lowered into the capillary which gives zero time of the experiment. For exact measurements of the function: activity versus time a RIDL 400-channel-analyzer was used, the channels being switched automatically by a timer. After background subtraction (and – if necessary – compensation for radioactive decay) the values are ready for plotting. The diffusion coefficients *(D)* are used for size *(r)* calculation according to Stokes-Einstein's relation:

$$r = \frac{kT}{6\pi\eta D}. \qquad (6)$$

Experiments

It seemed desirable to calibrate the method with particles of known grain size. For that purpose Al_2O_3 powder "Degussa 110-2/3" was used. The specific surface had been determined[8] as 51 m²/g indicating an average particle radius of 170 Å.

From an electronmicroscopic picture (41800×) the particle size distribution in an aqueous suspension could be counted directly, taking into consideration agglomeration to larger particles. The result is shown in Fig. 4 and yields a most probable radius of 250 Å.

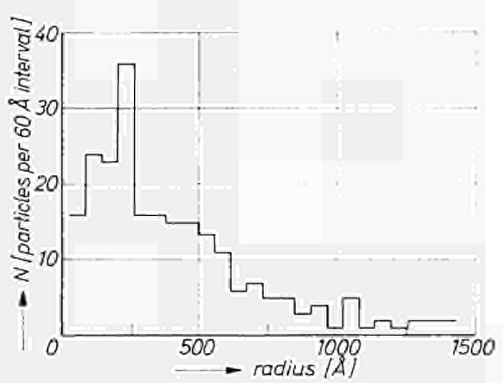

Fig. 4. Particle size distribution of Al_2O_3 powder

For the initial diffusion experiments the apparatus of Fig. 2 was used. The Al_2O_3 grains were tagged by immersion in 3 ml of a neutral Po-210 solution (0.3 μC/ml) for 1 hr under stirring.

The radioactive suspension was introduced into the diffusion capillary with a capillary pipette. The results of the radioactivity measurements are shown as curve A on Fig. 5.

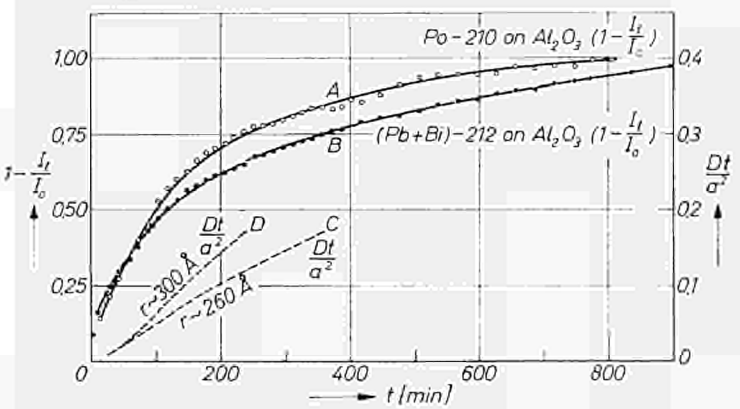

Fig. 5. Particle size determination by diffusion of Al_2O_3 tagged with Po-210 and (Pb+Bi)-212 resp.

The same figure contains as curve B the results obtained in the device of Fig. 3 after tagging Al_2O_3 with (Pb+Bi)-212. Using the graph of Fig. 1 the values for Dt/a^2 were obtained (curves C und D, which do not coincide because of different values for a). These curves are not perfectly straight, indicating that – instead of one grain size – a size distribution has been taken into account. Average grain size values calculated from D according to equation (6) are 300 and 260 Å, respectively, in fair accordance with Fig. 4.

After this calibration unknown particle sizes were determined in the latter device.

[6] O. Werner, Eine neue Methode zur Gewinnung hochkonzentrierter Emanationspräparate, Z. physik. Chem. **A 165**, 391 (1931).

Table 1. *Calibration and Size Determination by Diffusion of Radioactive Particles*

	Diffusionconst. D ($cm^2\,sec^{-1}$)	Capillary radius a (cm)	Particle radius r (Å)
Po-210 on Al_2O_3	$8.0 \cdot 10^{-8}$	0.085	300
(Pb + Bi) 212 on Al_2O_3	$9.4 \cdot 10^{-8}$	0.105	260
Po-210 radiocolloids	$3 \cdot 10^{-9}$	0.090	8000
(Pb + Bi) 212 radiocolloids	$1.8 \cdot 10^{-7}$	0.089	130

1. A pure Po-210 solution, produced by electrolysis from commercial (Radiochemical Centre, Amersham) solution on Pt and subsequent dissolution, was investigated (cf. curve A on Fig. 6 and values in Table 1).

2. Rn-220 was absorbed in very pure water as described above. Under these circumstances both Pb-212 and Bi-212 should form radiocolloids.
From the experience with Al_2O_3 it could be assumed that both nuclides would be absorbed on eventual carriers. The establishment of radioactive equilibrium between the two nuclides was checked. It was corrected for the decay of Pb-212 before plotting curve B of Fig. 6.

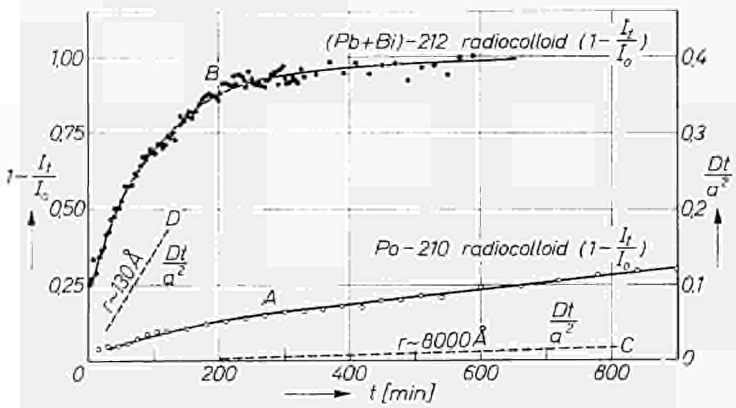

Fig. 6. Radiocolloid particle size determined by continuous diffusion measurements

Finally the radioactivity of these latter particles had to be estimated. The procedure has been described before[7]. 0.8 ml of the solution were filtered through a "Membranfilter ultrafein" and exposed to a nuclear emulsion plate (ILFORD K 1), which after development showed partically only single α-tracks and no star formation. This gives an upper value for the content in (Pb+Bi)-212 as measured by the α-radiation of Bi-212, Po-212 and Tl-208 when the initial radioactivity, the time of exposition and the decay rate is considered. It can be estimated that no particles with more than 60 initial Pb-212 atoms have existed.
The mass of a particle, however, as estimated from size and reasonable density, is equivalent to about 4.10^5 atoms, consequently the specific activity is probably as low as 10^{-4}.

Results and Discussion

The results of the typical determinations described above are condensed in Table 1.
The main result is that – in spite of many precautions – no carrierfree radiocolloids could be found. (Solid matter – though existing in the solution – is of very low concentration which can easily be determined this way). – It seems to us that the same situation has been prevailing in the majority of investigations in this field and that the proof for the eventual existence of "pure" radiocolloids in concentrations below the solubility product has still to be established. This may in principle be impossible in glass vessels exposed to α-radiation and future search may utilize organic materials with adsorbing surfaces.
Our work should not be confused with similar work on comparatively concentrated (10^{-7}–10^{-5} M) solutions of plutonium[9]. In the latter case colloidal particles of molecular weight 10^{10} have been found by autoradiography and such of MW 4.10^3 by diffusion. Obviously those two sets of measurement do not represent the same particles; the specific radioactivity is here probably equal to one, as to be expected for particles in solutions of concentrations above those of the solubility product. The genuine radiocolloid problem exists below those concentrations. –

[7] R. LINDNER, J. O. LILJENZIN und H. REINHARDT, Die Bestimmung der spezifischen Aktivität von Radiokolloidteilchen, Z. Elektrochem., Ber. Bunsenges. physik. Chem. **64**, 1059 (1960).
[8] R. LINDNER und HJ. MATZKE, Diffusion von Radon in Oxyden nach Rückstoßindizierung, Z. Naturforsch. **15a**, 1682 (1960).
[9] D. W. OCKENDEN and G. A. WELCH, Colloidal Quadrivalent Plutonium, J. Chem. Soc. [London] **1956**, 3358.