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Use of neutron-activation techniques for studying elemental distributions. Applications to geochemistry

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Abstract

The radiography method was developed for the investigation of the distribution of ionizing radiation sources on a sample surface by means of a two-dimensional image, produced in a photoemulsion or dielectric track detector. Its sensitivity is within the range 10^{-2}–10^{-7} g mm^{-2} with a resolution of from 0.01 to 100 μm. Statistical analysis and computer processing of the radiographic images have allowed us to solve the two main tasks of the method, namely the determination of the true distributions of ionizing radiation sources on a surface and the quantitative estimation of the local content of different chemical elements within a given accuracy. © 1998 Published by Elsevier Science S.A.

Keywords: Neutron irradiation; Photoexposure; Radiography; f-Radiography; Spatial distribution

1. Introduction

Nuclear-physical methods, giving detailed information on the content and structure of real objects, have a high sensitivity and accuracy for quantitative determination, which permits the set of soluble tasks to be expanded considerably. For the solution of urgent problems in various areas of physics, chemistry, geology, metallurgy, medicine, biology, agriculture and other branches of science and technology, it is necessary to obtain information on the spatial distribution of elements and their local concentration in additional to average content. Such information is important, for example, for objects containing elements in rather small quantities, which affect the physical, chemical and mechanical properties. A suite of radiographic techniques has been developed. We describe a theoretical model of radiographic image formation and a series of typical examples of using elaborate radiographic techniques to solve some practical problems.

2. Theory

Radiographic systems can be represented as three objects: an emulsion layer with thickness a, an interface layer of thickness h and a sample of thickness b with the radioactive sources distributed in it. Point coordinates of the sample have index m, and point coordinates of the photoemulsion have index n (Fig. 1). The distribution of radioactivity in a sample is described by the sample function $f(x_m,y_m,z_m)$ considered as two-dimensional. For all z_m the following equation is valid:

$$f(x_m,y_m,z_m)=\begin{cases} f(x_m,z_m), & 0\le y_m\le b \\ 0, & y_m<0 \\ 0, & b<y_m \end{cases} \quad (1)$$

The distribution of the number of developed silver grains on a radiogram can be described by the image function $f(x_n,y_n,z_n)$. The effect of radioactive atom ionizing radiation on a photoemulsion is determined by the absorbed dose and serves as a connection between the distribution of the number of developed silver grains in the photoemulsion and that of the radioactive atoms in the sample. The total absorbed energy in an emulsion element can obvious-

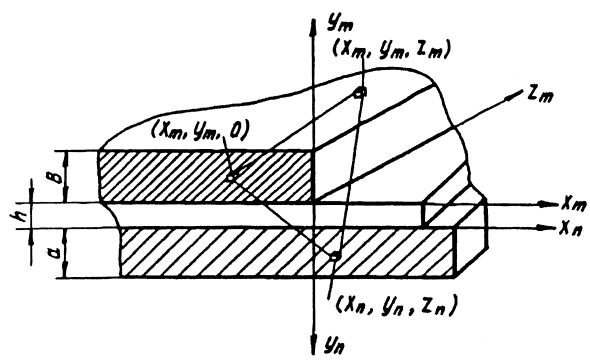

Fig. 1. Model of the radiographic system.

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ly be obtained by integration of the product of the dose absorbed in a point isotropic β-source $D(m,r)$ and the function of the distribution of the radioactive atoms in the sample $f(x_m,y_m,z_m)$ over the coordinates:

$$P(x_n,y_n,z_n) = \int_{-\infty-\infty}^{+\infty+\infty}\int_{0}^{b} D(\mu,r)f(x_m,z_m)\mathrm{d}x_m\,\mathrm{d}y_m\,\mathrm{d}z_m \quad (2)$$

$$r^2 = (x_n - x_m)^2 + (y_n + y_m + h)^2 + (z_n - z_m)^2 \quad (3)$$

According to the results of Ref. [1], the number of developed silver grains per unit square Z depends on the dose absorbed in the emulsion:

$$Z = Z_0\{1 - \exp(-kPb\rho/AZ_0)\} \quad (4)$$

where Z is the maximum number of developed silver grains per 1 μm of emulsion and A is the average energy expended per developed silver grain of a nuclear photoemulsion. For small values of $kPb\rho/AZ_0$ Eq. (4) transforms into

$$Z = kb\rho P/A \quad (5)$$

Practically, the most important case is when a linear dependence of the number of developed silver grains on the absorbed dose $D(\mu,r)$ is observed, as shown by Eq. (5). Then the distribution of developed silver grains in the radiogram is represented by the two-dimension integral equation

$$f(x_n,z_n) = \int_{-\infty-\infty}^{+\infty+\infty} f(x_m,z_m)K(x_n - x_m,z_n - z_m)\mathrm{d}x_m\,\mathrm{d}z_m \quad (6)$$

where

$$K(x_n - x_m,z_n - z_m) = \int_{0\,0}^{a\,b} D(\mu,r)\mathrm{d}y_m\,\mathrm{d}y_n \quad (7)$$

Eq. (6) has an approximate solution with the left-hand side as the function obtained with the help of an inverse Fourier transformation. Thus, knowing the particular experimental function for the distribution of the number of developed silver grains in a radiographic image, one can find the true distribution of the radioactive atom density in a sample. The model considered for the radiographic system contains the following assumptions:

1. the absence of self-absorption of radiation in the radioactive object;
2. the absence of radiation scattering in the photoemulsion;
3. the presence of a linear dose dependence of the developed silver grains, which is always observed for a short exposition time.

These assmptions are fulfilled for thin samples (up to 30 μm) and photoemulsion thicknesses of 1–5 μm. Thus, the image function $f(x_c)$ is determined as the irradiation dose received by the emulsion from the sources located in the sample, by the geometry of the radiographic system and by the physical–chemical characteristics of the detector and its treatment regimes. The basis for the calculation of the dose absorbed by the emulsion is the absorbed dose produced by a point radiation source in an homogeneous medium at distance r from the point radiation source. For a large number of β-radiators the absorbed dose $D(\mu,r)$ is determined by the relation

$$dD = \mu\bar{E}N\frac{\exp(-\mu r)}{4\pi r^2}dV_s \quad (8)$$

where E is the mean energy of the β-particles (keV), N the number of decays per 1 μm^3, dV_s the sample volume element (μm^3), μ the linear coefficient of absorption in the emulsion (μm^{-1}) and r the distance from the radiation source to the corresponding point in the photoemulsion (μm).

The application of radiography as a method for studying the chemical inhomogeneity in a thin structure is mostly limited by the accuracy of the reproduction of the distribution of the radioactive atom in the sample (the object function) and by the distribution of the photodarkness density or that of the developed crystals (the scatter function). For a few reasons, the scatter function cannot be identical to the object function. The radiographic image of a point source is not a point, because it includes the developed crystals located at different distances from the source. The distortion is caused by various factors related to the process of formation of hidden images and development of the emulsion. It is convenient to estimate the quality of image reproduction by the criteria of resolution, e.g., the minimal distance between activated sources, at which their radiographic images are separated. This criterion proposed in Ref. [2] is rather simple, direct and determined experimentally without any difficulty.

Let us consider the case of hard radiation, assuming the particle flux density from a point source to vary with distance by the inverse square law. Fig. 2 shows the relationship between the parameters of a sample-emulsion

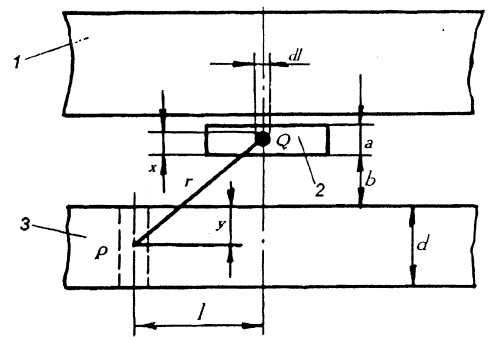

Fig. 2. Correlation between parameters of the radiographic system.

system, where the sample thickness is given by a, the distance between the sample and photolayer h, and the photoemulsion layer has thickness d. The irradiation point source Q is situated at distance x from the sample surface, and an arbitrary point of the photoemulsion P is situated at distance y from its surface. The dose accumulated at position P also depends on the activity of source Q. The density of the emulsion darkness is proportional to the number of developed crystals and, when the emulsion density is low, to the number of particles passing through an elementary volume of the emulsion. If the number of crystals dN arranged around point P and irradiated by the flux from source Q is within the emulsion volume $DV = dS\,\mathrm{d}y$ (where dS is the unit surface area of the emulsion), then

$$dN = dVA/r^2 = dSA\,\mathrm{d}y/r^2 \tag{9}$$

where A is the source activity. After integrating (9) over variable y, related to the emulsion thickness, within limits from 0 to d, we go to the elementary emulsion volume with thickness d:

$$dN = dS\int_0^d A\,\mathrm{d}y/r^2 = dSA\int_0^d \mathrm{d}y/l^2 + (y + b + x)^2 \tag{10}$$

Here, l is the linear distance of the elementary volume from the normal directed from point Q to the photoemulsion and dN is the number of developed crystals in the emulsion volume with thickness d and cross-section dS. However, the emulsion darkness density is dependent on the number of developed crystals per unit area of the surface layer, but independent of the total number of developed crystals. If one makes an additional integration of (10) over variable x, related to the sample thickness, from 0 to a, there will be a transition from point source Q to that with coordinate x from 0 to a:

$$d\tilde{N} = \frac{dN}{dS} = A\int_0^d \frac{\mathrm{d}y}{l^2 + (y + b + x)^2} \tag{11}$$

$$N = A\int_0^d \mathrm{d}x\int_0^d \mathrm{d}y/l^2 + (y + b + x)^2 \tag{12}$$

Calculating this integral for a thin sample ($a < d/10$) in direct contact with the emulsion ($b = 0$), we obtain

$$N = A[d/l\ \mathrm{arc\ tg}\ d/l - 1/2\ \ln(1 + d^2/l^2)] \tag{13}$$

As seen from (12), in this case the value of the linear resolution l (at constant A) is mainly determined by the characteristics of the emulsion. In spite of the limiting assumptions made in these calculations (ignoring absorption, scattering and rescattering) these conclusions are valid for radiation sources with energy ≥ 0.3 MeV. For isotopes with softer radiation, the scatter can be ignored.

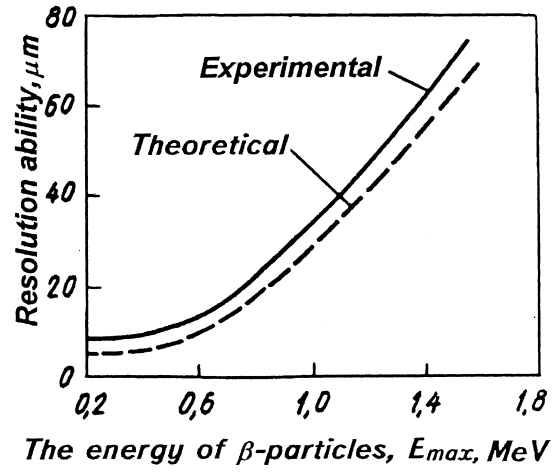

Fig. 3. The influence of radiation energy on the resolution.

The scattering function of a point source of $0.03 \leq E_\beta < 0.3$ MeV is

$$P_r = l^{-\mu r}/r^2 \tag{14}$$

where μ is the absorption coefficient depending on the radiation spectrum and absorber matter and r is the distance from the source. Using the expression for the scattering function of the sources within the energy range 0.03–0.3 MeV in the form of Eq. (13) and for isotopes with a harder radiation in the form of $P \approx 1/r^2$ we obtain the calculated value of the energy dependence of the resolution in the interval 0.2–1.6 MeV. The calculated data are shown in Fig. 3 (curve 1).

3. Experimental results

In addition, the energy dependence of the resolution was checked experimentally. Beta-radiators of different energies within 0.15–1.71 MeV were made using the following radionuclides: ^{35}S (167 keV), ^{45}Ca (258 keV), ^{60}Co (318 keV), ^{181}Hf (406 keV), ^{187}W (628 keV), ^{198}Au (960 keV), ^{122}Sb (1400 keV) and ^{32}P (1710 keV). Solutions of equal specific activity containing these radionuclides were passed through a column with the ion-exchange epoxy ''Dowex'' or ''AB-17''. After washing and drying, the epoxy was separated into fractions. The fraction containing the epoxy particles with sizes from 10 to 50 μm was placed on sticky tape as a thin layer. The prepared sources of different energies contacted the photoemulsion to obtain the radiograms. After photo measurement, the resolution was evaluated by widening of the radiographic edge of the separately taken grain images. As the energy increases from 0.2 to 1.7 MeV, the resolution becomes worse, at first slowly (from 5 to 9 μm) in the range 0.2–0.6 MeV, and then more rapidly (from 9 to 70 μm) within 0.6–1.7 MeV. Each experimental point is the aver-

age of more than 10 measurements. The obtained data are in good accordance with those calculated (Fig. 3, curve 2). Analyzing these data together with those available in the literature, one can conclude that the influence of the emulsion parameters is significant only when the resolution, depending on the geometry of the radiographic experiment and the energy of the studied radionuclei, is rather high, i.e. comparable to half of the sum of the initial and the developed crystals. Experimental data characterizing the dependence of the resolution on the system geometry and the emulsion parameters are listed in Table 1. Data characterizing the energy dependence of the resolution are listed in Table 2. All results were obtained with the emulsion MR.

Techniques of the local analysis of lead and zinc are based on fission and excitation reactions of the nuclei of these elements with radiographic registration of the fission fragments, α- and β-particles [3].

To study the dynamics of lead redistribution it is necessary to determine its local concentration at a level of 10^{-4}–10^{-5}% [4]. This is attainable by radiation with accelerated ^{16}O ions. The fission fragments of lead nuclei are registered during the irradiation. The $^{207}_{82}Pb(^{16}_{8}O,xn)^{233-x}_{90}Th$ reaction proceeds with the formation of fission fragments from Cd to Mo and Tc. On the other hand, during the process of thorium α-decay isotopes such as ^{212}Rn with a half-life of 23 min, ^{210}Rn ($T_{1/2}=2.7$ h) and others are formed. This allows us to apply α-radiography after irradiation. The fission tracks of lead were registered by a mica-muscovite detector and α-particles by cellulose nitrate. The ion source was a ^{16}O beam of 10 MeV/nucleon delivered by the isochronous cyclotron U-200 at the Joint Institute of Nuclear Research. During irradiation, the sample with the mica detector was fixed to a heat removing rotating metal disk. After irradiation the disk with sample was dismantled, the mica detector was removed for further processing and the activated sample was placed on cellulose nitrate to produce an α-radiogram. The temperature and time regimes of the detector processing are listed in Table 3.

The resolution does not exceed 10 μm for the fission track method and 20 μm for α-radiography. For evaluation of the local distribution of lead, the number of fission tracks (or α-particles) per area of detector of (25×25) μm^2 size was calculated. The area was calibrated by a lead nitrate standard.

The distribution of lead in a stratified sulphide-bituminous vein obtained with the use of the developed α-radiography technique is shown in Fig. 4. Fig. 5 shows the radiography of the lead distribution in dolomite on outlying galena macrocrystals produced by fission tracks.

The radiography of zinc was executed by activation of scale by thermal neutrons or fission neutrons in the nuclear reactor WWR-SM at the Institute of Nuclear Physics, Uzbekistan Academy of Sciences. Samples of rocks and ores were irradiated by a neutron flux of 10^{17}–10^{18} n nm^{-2} s^{-1}. The radioisotope ^{65}Zn generated by the reaction ^{64}Zn(n,γ)^{65}Zn has a half-life of 245 days, which is considerably longer than the half-life of other accompanying radioisotopes.

The sensitivity of the method for this element in natural mineral association is 10^{-6}%. The irradiated sample after ''cooling'' is implanted on sensitive photoemulsion FT-41, the photoblackening of which is related to the zinc content of the scale. Grains of sphalerite containing from 61 to 64% zinc (data for activation analysis) were used as the internal standard. Quantitative measurement of the photoblackening intensity of negatives was accomplished by a microdensitometer ''MD-100''. Neutron-activation radiography of the zinc distribution in siliceous dolomite is shown in Fig. 6.

Table 2
Influence of the radiation energy on the radiographic resolution of the MR emulsion

Isotope	Radiation energy, $E_{max\ \beta}$ (keV)	Resolution (μm)
^{35}S	0.167	15
^{187}W	0.628	30
^{198}Au	0.966	50
^{32}P	1.710	150

Table 1
The influence of the geometry of the system and the type of photoemulsion on the radiographic resolution

Isotope	Type of emulsion	Emulsion thickness (μm)	Interstitial layer thickness (μm)	Resolution (μm)
^{187}W	MR		0	2
		5–7	3	8.5
			10	14.5
^{187}W	X-ray film RT-1	15	0	30
^{187}W	X-ray film RM-1	24	0	40
^{35}S	''Micrat-300''	5	0	2.5
^{32}P	''Micrat-300''	5	0	15
^{35}S	FT-41	12	0	7.5
^{187}W	FT-41	12	0	15
^{32}P	FT-41	12	0	30

Table 3
The radiographic exposition and conditions of detector processing

Irradiation regime, integrated flux per sq.sm target	Mica-muscovite detector, tracks of fission fragments	Cellulose nitrate, tracks of α-particles
10^{15}	Annealing temperature 450°C for 5 h; etching in 40% HF for during 2 h at room temperature	''CR-39''plastic, 6 days exposure; etching in 40% NaOH for 1 h 40 min at 60°C
10^{14}	As above	Cellulose nitrate, 1 day exposure; etching in 40% NaOH for 50 min at 50°C

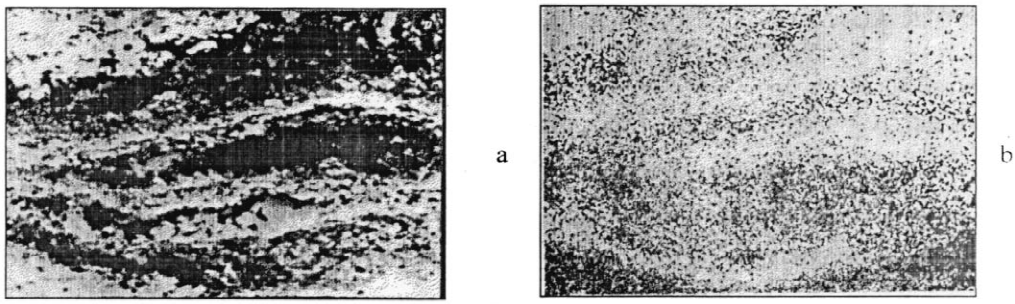

Fig. 4. The distribution of lead in a stratified sulfide-bituminous vein: (a) photograph in reflected light, ×200; (b) α-radiography on nitrocellulose CR-39.

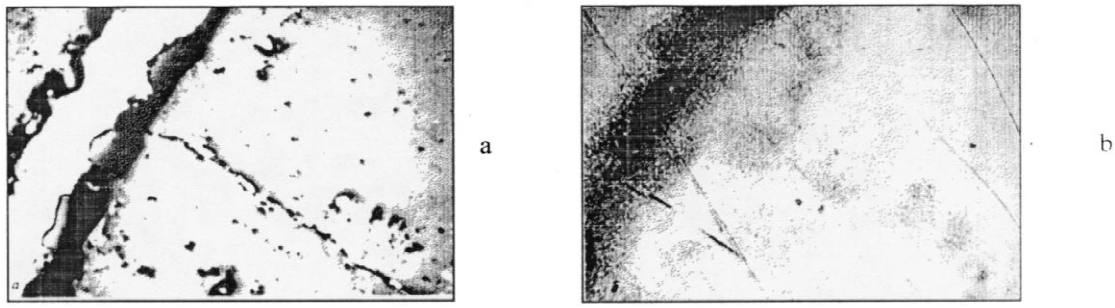

Fig. 5. The lead distribution in dolomite on an outlying galena macrocrystal: (a) photograph in reflected light, ×200; (b) radiography by fission tracks on mica-muscovite.

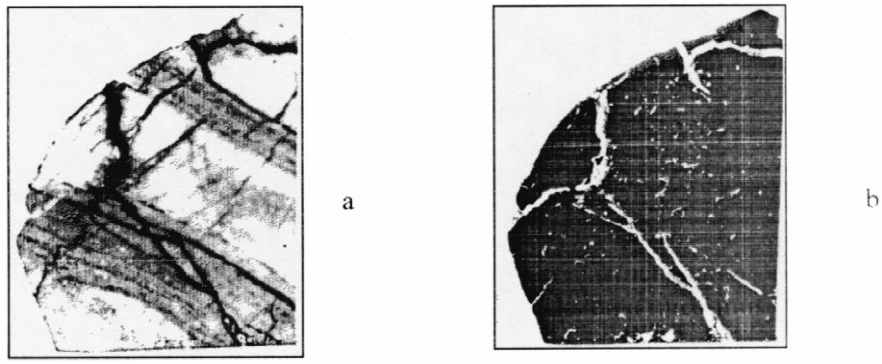

Fig. 6. The distribution of zinc in siliceous dolomite: (a) photograph of the scale; (b) neutron-activation radiography.

4. Conclusions

Based on the data obtained we conclude the following. Methods for local analyses of the lead and zinc concentrations in natural minerals have been developed with sensitivities of 10^{-4}–10^{-5} g mm^{-2} for lead and 10^{-6} g mm^{-2} for zinc. The spatial resolution of the methods is 7–10 μm for lead and 50–70 μm for zinc. A suite of radiographic techniques based on the registration of secondary radiation of neutron activated nuclei, instantaneous products of nuclear reactions and fission fragments of transuranium elements has been developed to solve a set of problems in geology and geochemistry, as well as for the analysis of technological and environmental samples.

References

[1] E. Odeblad, Lab. Invest. 8 (1959) 113.
[2] J. Donach, S.R. Pelc, Br. J. Radiol. 23 (1950) 184.
[3] G.N. Flerov, I.G. Berzina, Radiography of Minerals, Rocks and Ores, Atomizdat, Moscow, 1979.
[4] N.P. Ermolaev, V.P. Perelygin, E.S. Flitsiyan, Geochemistry 2 (1990) 195.