# Doping of AgHal Heterophase Microcrystals by $[IrCl_6]^{3-}$ Ions

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## Abstract

The influence of the doping of heterocontacting AgBr/AgBr(I) and AgBr/AgCl grains by $[IrCl_6]^{3-}$ ions on its photographic speed was investigated. Isometric and tabular crystals were used as a substrate. The incorporation of doping ions into the heterocontact zone was found to result in the change of the kinetics of photoinduced charge carriers interaction. The optimal doping ion concentration allows one to reveal the photographic speed increase and high-intensity reciprocal failure (HIRF) decrease. The photographic speed and HIRF values are shown to essentially depend on crystal habit. Based on the experimental data the phenomenological model of the photoprocess in doped heterophase AgHal microcrystals was suggested.

## Introduction

To optimize the photographic process in AgHal - photographic materials is possible by using the systems allowing us to increase the efficiency of the photoprocess at the expense of more effective utilization of the light energy the reduction of dispersion in an emulsion layer, the localization of latent images (LI) and the increase of the efficiency of the processes by chemical photographic processing of materials. AgHal grains with impurity ions are such systems. It is heavy metal ions that are more often incorporated into AgHal grains to govern their photographic properties.[1] The photoprocess in these grains is basically different from the process in usual ones. The presence of heavy metal ions results in grains impurity centers which are acceptors of electrons or holes. As a result, electrons and holes formed under exposition are trapped on them and are excluded from the process of a fast recombination. Slowing down of recombination processes results in the change of kinetic parameters of the photolysis of AgHal, processes of the formation of latent image centers (LIC) becoming preferable. Metal ions are most frequently introduced into AgCl grains as the formation of LIC in them proceeds slowly enough due to low ionic conductivity.[2]

The influence of $[IrX_6]^{3-}$ ions on photographic properties of emulsion grains is discussed in Refs. [3] and [4]. One of the first papers where the mechanisms of the influence of $[IrX_6]^{3-}$ ions were considered in detail is Ref. [5]. It was by a plenty of investigations of physical and photographic properties of followed doped with $[IrX_6]^{3-}$ ions grains having a various halide structure. Investigations of a luminescence[6,7] and TPC[8] allowed us to estimate an energy of Ir-centers. The influence of the location of $[IrX_6]^{3-}$ ions on ionic conductivity is discussed in Ref. [9]. However, the concentration of ions greatly exceeded the concentration used in photoemulsion grains. The life time of an electron trapped by the Ir-center increased when the concentration of $[IrCl_6]^{3-}$ in AgCl emulsions was more than $1,9 \cdot 10^{-7}$ mol Ir/mol Ag.[10,11] Also, binuclear complexes,[12] capable of irreversible or long-time trapping of electrons were assumed to be formed at greater concentrations. The complex $[IrCl_6]^{3-}$ ion in solution can dissociate, vacant coordination places being occupied by molecules of water. The embedding of the formed aqua complexes into the AgBr lattice according to Ref. [13] creates deeper electron traps. The regularity of the connection between the LIC formation and the localization of $[IrX_6]^{3-}$ in grain is shown in Ref. [14]. The influence of the habit of grains doped with $[IrX_6]^{3-}$ ions is investigated in Ref. [15]. However, that photographic properties were investigated on unsensitized emulsions leaves much uncertainty.

The goal of the present paper is to study the influence of impurity $[IrCl_6]^{3-}$ ions on photographic processes in AgBr grains of octahedron and cubic shapes, and in heterocontact isometric grains and tabular AgBr/AgBr(I) grains as well.

## Experiment

The preparation of silver halide emulsions was carried out by controllable two-jet crystallization. KHal and $AgNO_3$ solutions were poured into the reactor containing a required amount of an aqua-gelatin solution, at constant stirring. During the synthesis the temperature, the concentration of [Hal⁻] ions and the rate of pouring the solutions of reagents were regulated. A solution containing $[IrCl_6]^{3-}$ ions in the required concentration was poured at different stages of the synthesis, providing for their pre-determined localization in a microcrystal. The minimum volume of the $K_3[IrCl_6]$ solution was not less than 0,5 % from the total volume of the emulsion. After the process of the synthesis was over, the emulsion was washed off from soluble salts, pBr and pH values were brought to optimum values for sensitization. After sulfur-plus-gold sensitization, the emulsion was poured on a triacetate support and subjected to sensitometric tests.

## Results and Discussion

**Doping of AgBr Grains of Cubic and Octahedral Habit with [IrCl$_6$]$^{3-}$ Ions**

The analysis of sensitometric characteristics of the samples with cubic and octahedral grains with various localizations of [IrCl$_6$]$^{3-}$ ions showed that the greatest increase in photographic speed is observed when a dopant is located closer to the surface of the grains.

The dopant concentration was varied by incorporating the ions after 90 % of the AgNO$_3$ solution was added. The results obtained are presented in Fig. 1, 2.

Increase in photographic speed on octahedral and cubic AgBr grains is discussed in Ref. [15] where it is shown that the optimum concentration of [IrCl$_6$]$^{3-}$ ions for cubes is $10^{-7}$ mol/mol Ag and for octahedrons - $10^{-6}$ mol/mol Ag. The present authors determined that the amount increase of the dopant for unsensitized samples containing {111} grains (Fig. 1 a) results in the growth of the maximum optical density and does not appreciably influence the speed and optical density of the fog. Under sensitization (Fig. 1 b) the optimum concentration of [IrCl$_6$]$^{3-}$ ions is $1 \cdot 10^{-8}$ mol/mol Ag.
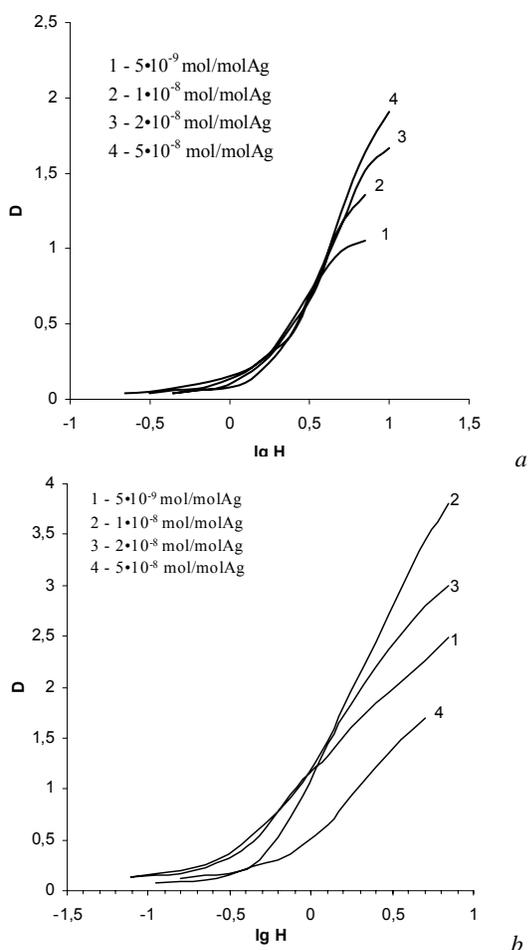




*Figure 1. Characteristic curves of emulsion layers containing AgBr {111} grains doped with [IrCl$_6$]$^{3-}$ ions: a – unsensitized; b – after a sulfur-plus-gold sensitization*
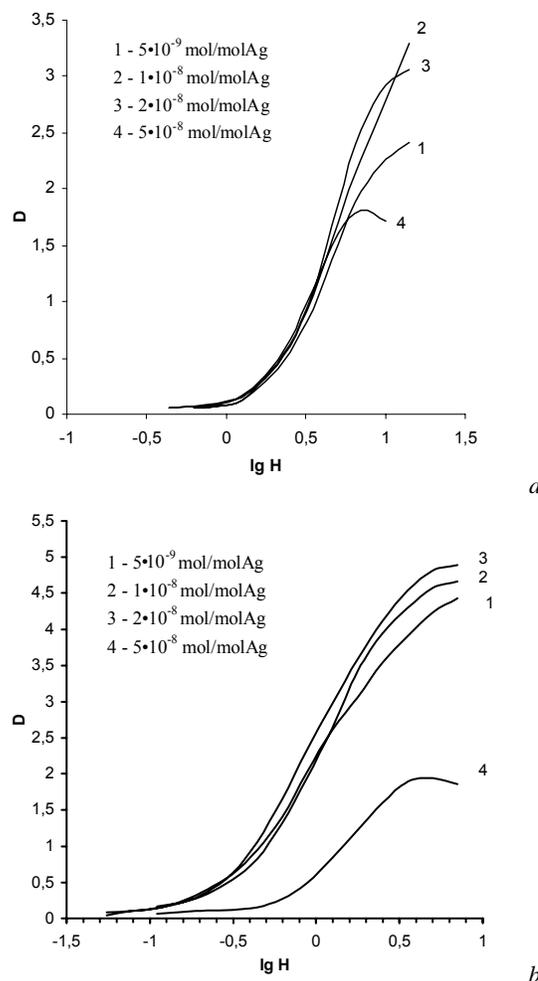




*Figure 2. Characteristic curves of emulsion layers containing AgBr {100} grains doped with [IrCl$_6$]$^{3-}$ ions: a - unsensitized; b – after a sulfur-gold sensitization*

For cubic grains (Fig. 2) the position of their characteristic curves does not change. However, at the concentration $5 \cdot 10^{-8}$ mol/mol Ag the process of desensitization is observed. To explain the observed effects it is necessary to consider the basic reactions proceeding during the formation of LIC in AgHal grains containing [IrCl$_6$]$^{3-}$ ions.

**The Basic Reactions During the Formation of LIC**

The Ir center in AgHal grains is capable of being a temporary trap for photoelectrons:

$$[Ir^{3+} \cdot 2Ag^-_\square] + e^- \leftrightarrow [Ir^{2+} \cdot 2Ag^-_\square] \qquad (1)$$
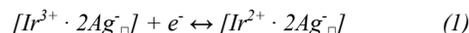
As a result, a trapped electron is excluded from the process of a fast recombination:

$$e^- + p^+ \rightarrow a \; recombination \qquad (2)$$

The capture of an electron by a trap created by chemical sensitization (CS) and the subsequent electrostatic attraction of an interstitial Ag$^+$ ion result in an Ag$^0$ atom and

this process is repeated many times until the formation of LIC $(Ag_n^0)$:

$$e^- + Ag_I^+ \leftrightarrow Ag^0 \rightarrow Ag_n^0 \qquad (3)$$
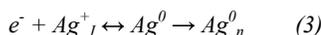
Electrons temporarily trapped by the Ir center and thus excluded from the recombination processes take part in the formation of LIC (reaction 3). As a result of regeneration (since reaction 1 is reversible) the Ir-center can act as an electron trap again.

Irreversible decay of the latent image:

$$Ag_n \rightarrow nAg^+ + ne^- \qquad (4)$$
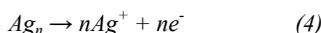
The following reaction can take place:

reversible trapping of the hole with the formation of the V-center

$$[Ir^{3+} \cdot 2Ag^-_\square] + p^+ \leftrightarrow [Ir^{3+} \cdot Ag^-_\square \cdot V] \qquad (5)$$
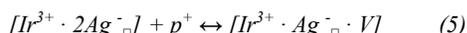
The movement of the hole is essentially slowed down and, therefore, electron-ionic processes of the formation of the latent image (LI) can be completed before the hole has diffused to the site of the LIC formation. Besides, owing to the neutral charge of the V-center the probability of Coulomb interactions of the hole with the trapped photoelectron decreases.

The process of ionizing the complex is possible when the cation vacancy leaves the complex[16]:

$$[Ir^{3+} \cdot 2Ag^-_\square] \leftrightarrow [Ir^{3+} \cdot Ag^-_\square] + Ag^-_\square \qquad (6)$$
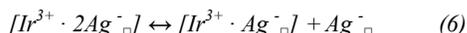
As a result, the efficiency of trapping the electrons increases.[17]

**Effects of Increase in Photographic Speed and the Reduction of Deviations from the Reciprocity Law**

As was mentioned above, the incorporation of $[IrCl_6]^{3-}$ ions into the AgHal crystalline lattice results in electron traps capable of a reversible capture of electrons (reaction 1). Thermo-induced transfer of electrons from the Ir traps into the conductivity band contributes to the increase of the duration of the electronic stage of LIC formation. As seen from Fig. 3, the photographic speed at expositions < 0,05s considerably increases.

At intensive exposures to light, Ir centers act as temporary traps of electrons, with the exception of processes of fast recombination and the capture of electrons on smaller centers of photographic speed. Both photoelectrons and electrons got into the conductivity band due to thermo-induced transfer from Ir-centers take part in LIC formation (reaction 3).

At less intensive exposures the increase in photographic speed is due to the accepting of all or some holes by their cationic vacancies (reaction 5). Thus, holes are excluded from the processes of recombination and oxidation of LI centers and latent subimage centers by molecular bromine, which, in the opinion of Mitchell,[18] is the main reason for the decrease in photographic speed.
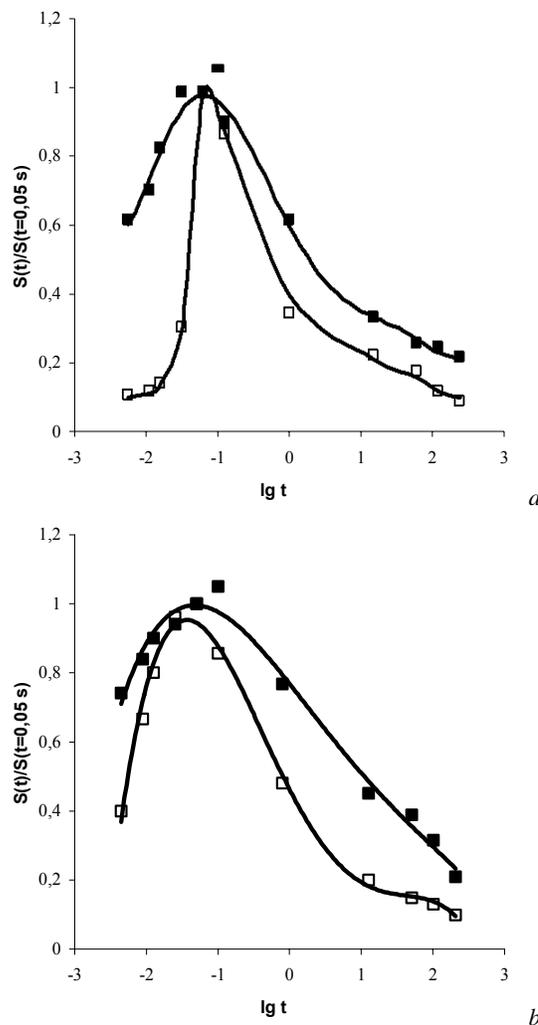


*Figure 3. Dependence of relative photographic speed from exposure time for AgBr grains (□ – pure; ■ – doped $[IrCl_6]^{3-}$ ions): a - {111} C ($[IrCl_6]^{3-}$) - $1 \cdot 10^{-8}$ mol/mol Ag; b - {100} C ($[IrCl_6]^{3-}$) - $2 \cdot 10^{-8}$ mol/mol Ag*

**Doping of Heterocontact AgBr/AgCl Epitaxial Grains**

A great number of dislocations are known to be formed due to the contact of phases with lattices of various structures. Dislocations along the heterocontact are capable of being positively charged due to the translation of holes from the AgCl phase to the heterocontact,[19] and probably serving as electron traps. Besides, there is a decrease in the efficiency of the recombination process due to a spacious separation of photoelectrons and holes. The heterocontact in these grains can be an effective center of latent image formation. However, recombination processes of photoinduced interface charge carriers cannot be excluded.

Therefore, to investigate the influence of $[IrCl_6]^{3-}$ ions on the photoprocess in AgBr/AgCl heterocontact grains is of interest. The dependence of relative photographic speed from the exposure time for these systems is presented in Fig. 4.
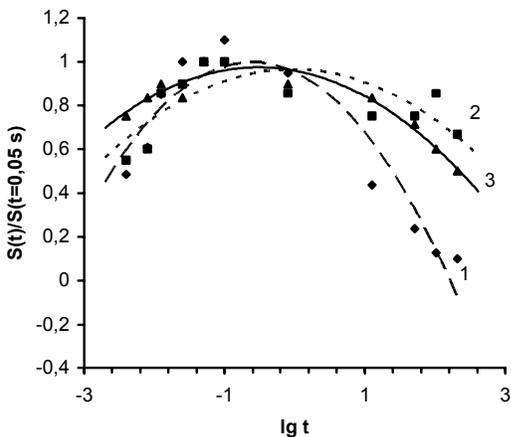
*Figure 4. Dependence of relative photographic speed from exposure time for emulsion layers containing AgBr grains: 1 - {100}; 2 - {100} with AgCl epitaxes; 3 - {100} with AgCl epitaxes (doped with $[IrCl_6]^{3-}$ ions)*
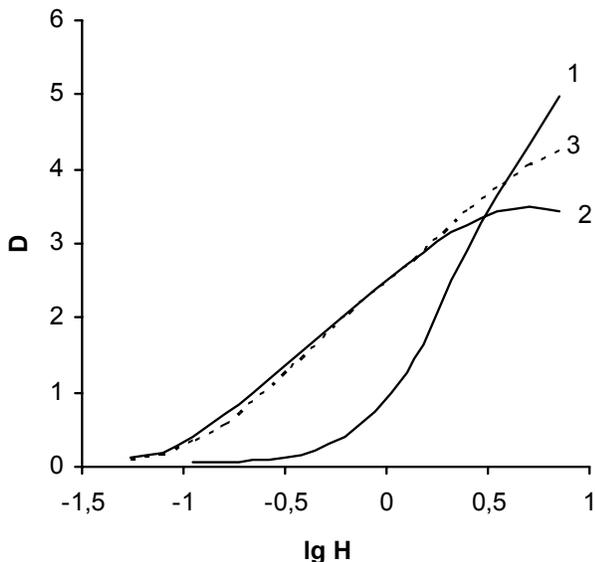


*Figure 5. Characteristic curves of emulsion layers with AgBr grains : 1 - {100}; 2 - {100} with AgCl epitaxes; 3 - {100} with AgCl epitaxes (doped with $[IrCl_6]^{3-}$ ions)*

As seen from Fig. 4 decrease in photographic speed in lgt > 0 range for AgBr/AgCl epitaxial grains is less intensive than for cubic AgBr grains. The heterocontact area is likely to be an effective center for concentrating the photolysis products excluding or slowing down the processes of thermal decomposition of the smallest photolytic silver particles. The translation of holes is due to the different energies of the conduction band bottom and the valence band top between AgBr and AgCl phases, it resulting in spacious separation of photoelectrons and holes in the heterocontact zone. This, in its turn, makes the recombination of photoinduced charges carriers low

probable. In the range of smaller exposures, the slope of relative photographic speed curve does not change. The incorporation of the dopant into the heterocontact zone results in the reduction of the slope of relative photographic speed curve in the lgt < 0 range. The life time of electrons in the conductivity band increases up to the time required for LIC formation owing to Ir-centers.

**Doping of Heterocontact Tabular AgBr/AgBr(I) Grains**
The distribution of impurity ions in the bulk of tabular grains incorporated at various stages of the growth of grains in contrast to isometric grains is not clear. It is impossible to use the same approach for tabular and isometric grains and the distance from Ir-centers in the bulk of tabular grains to the surface as a criterion. The distribution of $[IrCl_6]^{3-}$ ions in tabular grains is possible as a shell on the entire surface, or preferably in the lateral shell. The distribution of the dopant depends on the conditions of synthesis. The present authors carried out a number of experiments on incorporating the $[IrCl_6]^{3-}$ ions at various stages of the growth of tabular grains consisting of the AgBr core and the $AgBr_{0,96}I_{0,04}$ shell. The synthesis was carried out at T = 60 ºC and pAg = 10,7-11,1. Impurity ions were incorporated into the core and the shell and into the heterocontact zone as well. Characteristic curves of the obtained samples are presented in Fig. 6.
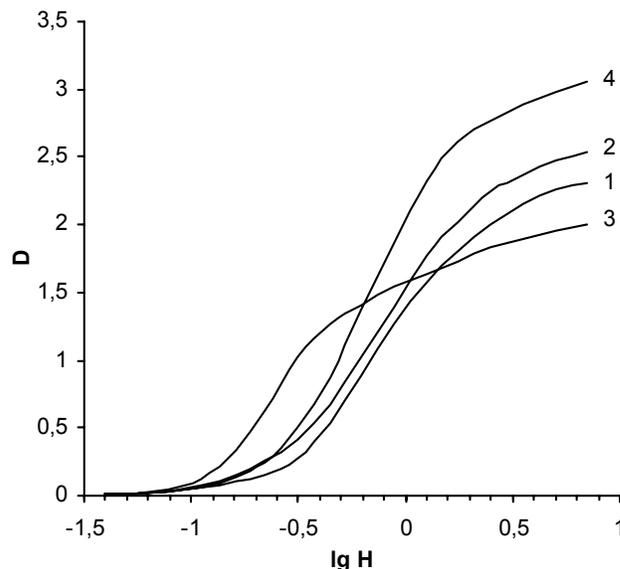


*Figure 6. Characteristic curves of emulsion layers on the basis of tabular AgBr/AgBr(I) grains with different localizations of $[IrCl_6]^{3-}$ ions: 1 – undoped; 2 – in the AgBr core; 3 – in the heterocontact; 4 – in the AgBr(I) shell*
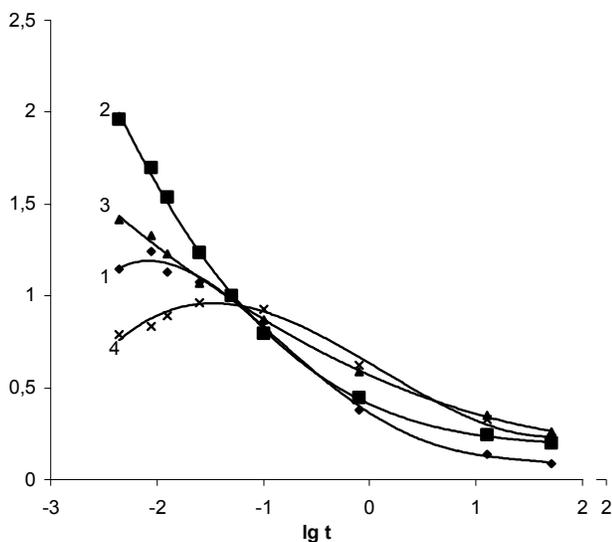
*Figure 7. Relative photographic speed of tabular AgBr/AgBr (I) grains with various localizations of $[IrCl_6]^{3-}$ ions vs. exposure time\*: 1 – undoped; 2 – in the AgBr core; 3 – in the heterocontact; 4 – in the AgBr(I) shell*

The use of the heterocontact, due to different energies of the conduction band bottom and the valence band top of these phases allows one to make the directed translation of photoinduced charge carriers possible. Thus, the energy of incident light can be used more effectively, in comparison with homogeneous grains.

During the contact of the two phases and the alignment of Fermi levels in these phases, there is a bend of energy bands on the boundary, its value being 0,2 eV.[19] Hence, low-energy electrons constituting a greater part of electrons transferred into the conductivity band are unable of direct transition from the AgBr in AgBr (I) conductivity band. The translation of photoelectrons through the heterocontact has been assumed to be carried out through small electron traps in the forbidden band.[20] Small electron traps are formed on structural or impurity defects. The $[IrCl_6]^{3-}$ impurity ion can be such a defect. Therefore, the oriented translation of photoinduced charges can be affected by the incorporation of ions. Electrons trapped in the heterocontact area are likely to participate in the LIC formation on the boundary.

When an impurity $[IrCl_6]^{3-}$ ion is incorporated into the AgBr core (Fig. 6, 7 curve 2) photographic speed is increased, particularly in the area of short time exposure. In this case it is possible to optimize the photoprocess in the vicinity of the photographic speed center as photographic speed centers and LIC are known to be formed in the core. The size distribution of the LIC changes due to the temporal accepting of photoelectrons by Ir-centers.

The incorporation of $[IrCl_6]^{3-}$ ions into the heterocontact area (Fig. 6, 7 curve 3) is particularly effective. In this case the increase in photographic speed is accompanied by significant maximum optical density decrease, thus confirming the LIC number decrease on the surface of grains.

Optical density is maximal for the doped AgBr(I) shell (Fig. 6, 7 curve 4), photographic speed having its maximal value when t = 0,025 s, it being insignificantly dependent on exposure time.

*\*Our experimental data on photographic speed (Fig. 7) require corrections in a greater range of exposures (10-2 – 10-6 s). In this range, curves 1, 2, 3 must have an extremum. Unfortunately, the available equipment does not allow us to carry out this research.*

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## Biography

**Boris A. Sechkarev** was born in Kemerovo (Russia) on August 3, 1955. In 1978 graduated from the Moscow State Pedagogical University, Physical Department. Since 1979 he works on Kemerovo State University. Now Boris A. Sechkarev is Vice-Rector of the University, Professor and Head of Chemical Physic Chair. Doctor of Chemistry since 1999. Field of scientific interests includes the different problems of photographic chemistry of silver halides. He is the author of more than 100 scientific publications.