

# Determination of the Silver Sulphide Cluster Size Distribution via Computer Simulations

*E. Charlier, R. Gijbels*

*University of Antwerp (UIA), Department of Chemistry  
Antwerp, Belgium*

*M. Van Doorselaer, R. De Keyzer  
Agfa-Gevaert N.V., R&D Laboratories  
Mortsel, Belgium*

## Abstract

Addition of a labile sulphur donor to light sensitive silver halide microcrystals results in the formation of a distribution of silver sulphide clusters on the crystal surface. These silver sulphide clusters enhance the efficiency of image formation during the photographic process. Their activity towards the capturing of light photons, however, is very critical to their size (aggregation number) and concentration. By incorporating gold ions into silver sulphide clusters it was possible to monitor the size distribution by measuring the amount of gold reacted. From these experiments, no evidence was found for aggregation of the reacted sulphur entities on the surface. The uptake of gold ions at different sulphur concentrations could well be fitted with a simulated size distribution when a catalyzed deposition of sulphur was assumed, with a reactivity of the surface equal to 1.0 % for the microcrystals studied. From a simulation of the silver sulphide cluster size distribution a correlation could also be found between increasing aggregation numbers and the absorption at increasing wavelengths in diffuse reflectance spectroscopy.

## Introduction

From the first observations made on silver sulphide clusters it was concluded that silver sulphide specks were present on the silver halide surface, formed by aggregation and catalysed deposition of silver sulphide clusters. Recent investigations have shown that sensitivity may be caused only by dimers of sulphide<sup>1,2</sup>, hence determination of the fraction of sulphide clusters with a specific size is useful to obtain information about the distribution of sensitivity centers and the rearrangement process on the crystal surface. In 1979, Sturmer and Blackburn<sup>3</sup> used a statistical approach on the sulphur deposition and came to the conclusion that the number of dimers formed at optimal sensitivity is situated around 200 per  $\mu\text{m}^2$ . This low aggregation number of sensitivity centers already indicates that aggregation is a doubtful step in the sensitisation process; however, a lot of the ex-

perimental data are still considered to be due to aggregation of reacted sulphide at the surface<sup>4,5</sup>. Most of these data change considerably as a function of ripening time; from photographically not sensitive towards sensitive<sup>2</sup>, from hole trap towards electron trap<sup>6</sup>, no absorption at specific wavelengths to absorption. This transition is explained by the aggregation of single sulphide into larger sulphide aggregates, but is interpreted in our model<sup>7</sup> by the supply of silver interstitial ions towards the deposited sulphide clusters.

From other experiments it could be concluded that gold ions could only be incorporated in silver sulphide clusters when at least 2 sulphur ions are present<sup>8-10</sup>. From this information one knows exactly the ratio between isolated reacted sulphur atoms (monomers) and higher silver sulphide aggregates. When this ratio was monitored as a function of reaction time, we found after a certain saturation time no increase in gold uptake<sup>11,12</sup>. One thus could conclude that, as a possible alternative to the migration process, reacted sulphide atoms stay on their location on the silver halide surface after deposition and the cluster can only be formed by the deposition of other sulphur atoms on a neighboring surface position.

However, when gold ions are added to the emulsion it catalyses the deposition of silver sulphide ions itself, by deposition of gold silver sulphide, resulting in a change in cluster distribution. For this reason we used a fast sulphur donor with a high yield; so the uptake of afterwards added gold can only be due to the reaction of gold on the silver sulphide clusters. The ratio between monomers and multimers gives us vital information about the size distribution of the  $\text{Ag}_2\text{S}$  clusters on the surface of the silver halide microcrystals. A computer program was written in which the size distribution could be simulated for different number of sulphur atoms, crystal sizes and different reactive spots on the surface itself. The gold uptake on these simulated distributions was then compared to the experimentally obtained gold values. From these results not only the size distribution could be determined, but also the reactivity of the surface towards sulphur ions.

## Experimental

Silver bromide octahedral microcrystals of 0.4  $\mu\text{m}$  (mean edge length) were prepared as a suspension by the controlled double-jet method and suspended in aqueous gelatin. The emulsion was diluted until a concentration of 0.883 mol Ag / kg of emulsion was reached. The pH and pAg of the emulsion were adjusted for each reaction vessel at a total weight of 130 g. The emulsion was further diluted to a total weight of 150 g minus addenda. The concentration of gelatin was 0.5 g / g  $\text{AgNO}_3$ . In order to form the silver sulphide clusters on the surface diacetyl thiourea was added to the emulsion and the temperature was raised. By using diacetyl thiourea the sulphur deposition goes fast with a high yield of circa 92 %, resulting in a fixed cluster distribution on the surface<sup>12</sup>. At different time intervals, 1.75 ml of the emulsion was taken and coated on a glass plate of 3 x 3  $\text{cm}^2$  pre-coated with a gelatin layer of 1  $\mu\text{m}$  containing hardeners. Under these conditions the infinite thickness is reached for both tracer measurements and registration of diffuse reflectance spectra DRS. Diffuse reflectance spectra of the coated emulsions were measured after drying overnight. The coated layers (circa 250  $\mu\text{m}$  thick) were placed against the integrating sphere of a Shimadzu UV-3101-PC spectrophotometer using the white stone spectralon (from Optilas) as a reference. In this configuration the background for unsensitized emulsions was equal to  $0.0135 \pm 0.0002$  in absorption units in the wavelength region of 500 - 900 nm. Due to the low absorption of the  $\text{AgX}$  crystal in this region and the low scattering of the silver sulphide clusters, the obtained spectra may be converted from reflectance ( $R_\infty$ ) to Kubelka-Munk (KM) values<sup>13</sup>:

$$KM = \frac{(I - R_\infty)^2}{2R_\infty} \quad (1)$$

Since the KM spectrum is linearly proportional to the concentration under these conditions<sup>14</sup>, subtraction of the unsensitized emulsion from the sensitized emulsion results in a new KM spectrum, which is proportional to the concentration of silver sulphide only<sup>15</sup>. Independent on the concentration of sulphur, the reaction conditions and the morphology of the silver halide grains, all the obtained spectra could be deconvoluted with a minimum of three Gaussian curves with a maximum at 2.46 eV (505 nm), 2.20 eV (560 nm) and 2.00 eV (620 nm) and with constant width at half peak height<sup>7,11</sup>. In our view, these energy levels correspond with different sizes of clusters, where small clusters absorb at high energy and larger clusters at lower energies<sup>11</sup>. All KM values at specific wavelengths mentioned in this paper are the peak values obtained via deconvolution of the spectra.

The number of gold atoms that reacted with the formed silver sulphide clusters was measured via tracer analysis. We used  $\text{H}^{198}\text{AuCl}_4$  as reagent, which emits beta radiation with an average energy of 0.962 MeV and a decay time of 2.964 days<sup>16</sup>. The treatment of the emulsion was identical to the non-labelled gold component. After the reaction 10 mmole  $\text{KSCN}$  / mole Ag was added to remove gold ions incorporated between a sulphur atom and a silver atom of the  $\text{AgBr}$

lattice<sup>10</sup>. The quantity of these substitutional gold ions is not proportional to the cluster size distribution. After another 60 minutes of reaction time the emulsion was coated on glass plates as described above and washed 3 times with a  $\text{Na}_2\text{SO}_3$  (0.01 M) and alanine (0.01 M) solution for 18 hours to remove the unreacted gold ions. This washing step is not executed for the DRS sample preparation method, since unreacted compounds do not absorb in the wavelength region of interest. The emulsion was then dried and the beta activity measured with a proportional counter (Canberra 2404 alpha / beta counter) and compared to the unwashed emulsion. Corrections were made for background radiation and wash efficiencies. The detection limit depends on the specific activity of the radioactive tracer and attains  $2 \text{ E-8}$  mole Au / mole Ag under optimal conditions.

## Results and discussion

By assuming that there is no aggregation of sulphide molecules by surface diffusion, one can simulate the silver sulphide cluster distribution numerically via random deposition of sulphur clusters on the surface. When comparing the reaction rate of sulphur deposition on octahedral and cubic crystals it was clear that sulphur ions are deposited preferentially at (111) faces of the crystal or positive kink sites on the surface<sup>17</sup>. To simulate this hexagonal (111) surface, a matrix was constructed to represent this surface. A part of this matrix is shown in figure 1, where X represents reactive spots for sulphur atoms. Normally this matrix should contain between each row another row of zero's, but these are deleted to minimize the size of the matrix. To determine the dimensions of this matrix, which represents the whole surface of a 0.4  $\mu\text{m}$  octahedral crystal, one can define a unit cell on the (111) surface by a rectangle of 4.08  $\text{\AA}$  by 7.06  $\text{\AA}$ , with 4 sulphur atoms at each corner and one in the middle. Taking into account the surface of the crystal one can calculate that there are 4.12 E6 possible reactive sites on one octahedral crystal of 0.4  $\mu\text{m}$ . Since our matrix has as many reactive (X) as non-reactive sites (0) (see Figure 1), the complete surface of one crystal can be simulated with a matrix of dimension 8.25 E6 (= 2 x 4.12 E6). The matrix represented in figure 1 is a distortion of the actual hexagonal structure, so one has to remember that the maximum number of neighbouring surface cells, where a sulphur atom can react, is actually equal to six.

```

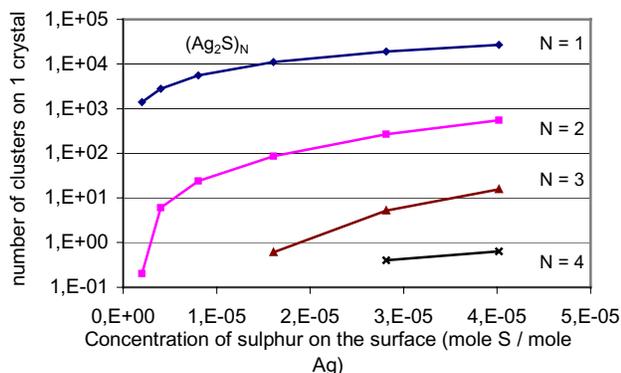
X 0 X 0 X 0 X 0
0 X 0 X 0 X 0 X
X 0 X 0 X 0 X 0
0 X 0 X 0 X 0 X
X 0 X 0 X 0 X 0
0 X 0 X 0 X 0 X
X 0 X 0 X 0 X 0
0 X 0 X 0 X 0 X

```

Figure 1. Starting condition of the matrix used to simulate the cluster size distribution; X = possible reaction positions for sulphide ions

The optimal photographic sensitivity was found at a sulphur concentration of  $1.2 \times 10^{-5}$  mole S / mole Ag reacted on the surface. Since one octahedral crystal of  $0.4 \mu\text{m}$  contains  $1.16 \times 10^{-15}$  mole Ag, the number of sulphur atoms on one crystal can be calculated to be equal to 8382 atoms for the optimal activity (i.e. a surface coverage of 0.21 %). After the dimension of the matrix is set, a random location on that matrix is selected for each sulphur atom, which corresponds to the possible reactive sites on the surface (X in figure 1). The initial value of zero of the location is set to 1 upon reaction. After each sulphur atom is deposited, the values of the neighbouring possible reactive sites are checked to determine the size of the deposited cluster. A stable cluster size distribution was reached under all conditions when the total number of atoms simulated was equal to  $2 \times 10^5$  (i.e. number of iterations  $\times$  atoms deposited during each iteration).

An example of the silver sulphide cluster size distribution obtained according to this method as a function of the reacted sulphur concentration reacted is represented in figure 2. At low sulphur concentrations monomers of silver sulphide are predominantly formed, while at higher concentrations first dimers and later on trimers and quadrimers appear.

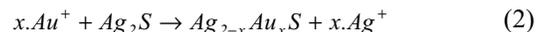


**Figure 2.** Simulated concentration of sulphur clusters for a specified cluster size on 1 crystal (sites =  $4.21 \times 10^5$ , atoms  $\times$  iterations =  $1.4 \times 10^5$ , octahedral crystals of  $0.4 \mu\text{m}$ , reactivity surface = 100 %)

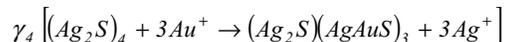
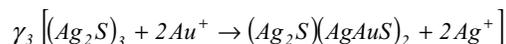
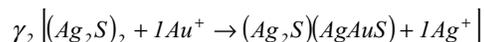
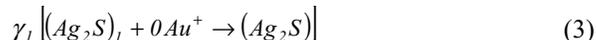
#### Determination of the number of gold ions incorporated

This simulation of the size distribution can now be confronted with experimental results of the gold uptake. In order to do so, one has to determine the maximum uptake of gold ions in the different aggregates of silver sulphide clusters. For a dimer of sulphur it is clear that only one gold ion can be positioned between the two sulphur atoms. For higher cluster forms it becomes more difficult. To obtain the uptake values for larger clusters we changed our simulation program to derive the average number of gold ions that can be epitaxially built in. The results of these simulations were surprisingly simple. For a silver sulphide cluster with aggregation number  $N$ , the average number of gold ions that can be incorporated is equal to  $N - 1$ . Instead of the general

equation used in photographic science for the building in of gold into silver sulphide clusters:



one should make a distinction between the concentration of each aggregation number of the silver sulphide clusters:



where  $\gamma_N$  represents the concentration of different aggregates ( $N$ ). At each reacted sulphur concentration it is now possible to calculate the number of gold ions that can be incorporated according to equations 3. For the simulated size distribution at the highest concentration in figure 2 ( $4.0 \times 10^{-5}$  mole S / mole Ag) the gold uptake value was calculated and found to be equal to  $6.2 \times 10^{-7}$  mole Au / mole Ag, while the experimental value was 17 times higher ( $1.0 \times 10^{-5}$  mole Au / mole Ag). This means that in our simulated deposition model the number of higher aggregates is much too low. Therefore modifications were made to the simulation program.

#### Modifications in the cluster deposition model

When a sulphide ion is deposited on the surface, silver ions from the solution or the crystals are attracted to this site (monomer) to form complete epitaxially grown cells. When initially one silver ion (reactive site) was present on the surface, reaction of sulphur resulted in the supply of 2 extra silver atoms. Therefore, in our modified simulation the deposition of a sulphur atom creates two other reactive sites next to it, thus promoting adjacent deposition of sulphur ions. In the program this is achieved by converting a non-reactive site (value '-1') to a reactive one (value '0'). Without catalysed deposition the cluster size is completely determined by the random distribution of the reactive sites on the surface.

Secondly, under our experimental conditions the free silver concentration in solution is equal to  $3.28 \times 10^{-9}$  M and the free bromide concentration  $7.05 \times 10^{-4}$  M. This means that the (111)-face of the octahedral crystal is mostly covered with bromide ions, which are not reactive towards sulphide deposition. This bromide surface is not perfect but there will be some reactive spots; silver ions, positive kink sites, ... To simulate these bromide ions a value of '-1' is given to random matrix elements. If one defines that 50 % of the (111) surface is covered with bromide ions, then 50 % of the reactive sites will randomly be converted into -1. If one would simulate this by reducing the matrix with 50 % the size distribution will be altered, but this would not correspond with the random position of kink sites. Consequently, another parameter is introduced in the simulation program, namely the surface reactivity. This surface reactivity can thus be defined as the percentage of reactive kink sites (silver ions) on the surface over the total number of surface sites. It is

clear that a lower surface reactivity results in a size distribution where the higher cluster forms are more dominantly present.

In figure 3 the experimental gold uptake, represented by the points with error bars, is shown as a function of the sulphur concentration added. The dotted lines represent the gold uptake values simulated for different surface reactivities with catalysed deposition. When the surface is completely reactive (100 %), the simulated gold uptake is much too low as already mentioned above. A very good agreement between simulated and experimental values could be found for a surface reactivity of 1.0 %. Note how much the simulated uptake value changes for surface reactivities around 1 % and lower. Since we now know the surface reactivity for our crystal system, we can calculate back the size distributions as a function of the sulphur concentration.

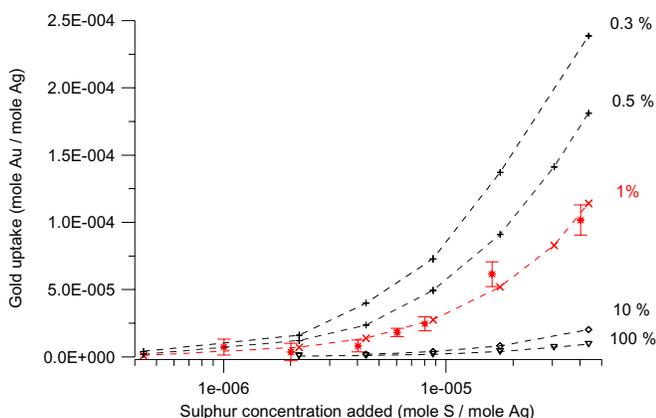


Figure 3. Gold uptake as a function of the sulphur concentration added (points with error bars = experimental data, dotted lines = simulations at different percentages of surface reactivity)

In figure 4 the absolute number of silver sulphide clusters with a specific size on a single crystal is plotted as a function of the sulphur concentration added (cfr. figure 2 for a surface reactivity of 100 % and no catalysed deposition). Under this deposition model the size distribution is much more shifted towards the higher aggregation numbers. At optimal photographic sensitivity, which is obtained for  $1.2 \text{ E-}5$  mole S / mole Ag on the surface, in our simulated size distribution 81 % is present as monomer, 17 % as dimer and the rest fraction of 1.8 % as trimers and quadrimers. When we calculate the absolute number of dimers we find a number of 466 per crystal or 785 dimers per  $\mu\text{m}^2$ . Keevert and Gokhale<sup>2</sup> could fit their sensitometric data when 1000 dimers per  $\mu\text{m}^2$  are present, where the centers containing two sulphur atoms make the largest contribution to photographic speed. However, they assumed that single reacted sulphide atoms aggregate to form large sulphide aggregates according to Smoluchowski's equation<sup>18</sup>.

Since the sulphur size distribution is highly dependent on the arrangement of the silver halide surface, small changes in the reaction environment can have large effects

on this distribution and thus on the gold uptake. This also explains the relatively large errors obtained for repeatedly executed gold uptake measurements.

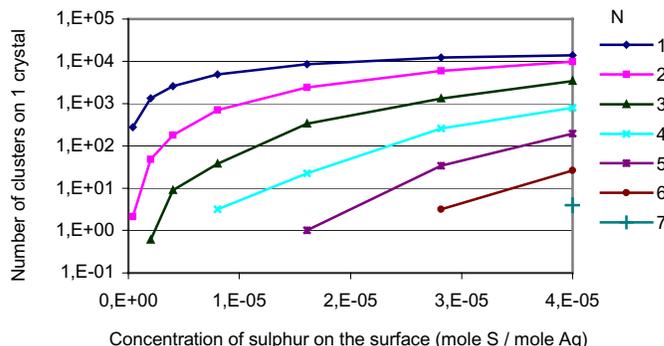


Figure 4. Simulated size distribution on 1 crystal (sites =  $4.21 \text{ E}5$ , atoms  $\times$  iterations =  $1.4 \text{ E}5$ , octahedral of  $0.4 \mu\text{m}$ , reactivity surface = 1.0 %)

#### Correlation between simulations and optical spectra

Since it is assumed that the absorption at 505 nm, 560 nm and 620 nm observed by diffuse reflectance spectroscopy (DRS) is caused by specific cluster sizes, one can try to find a correlation between the concentration and KM intensity. Via tracer analysis the reacted sulphide concentration can be determined at different time intervals. From these values the silver sulphide cluster size distribution can be calculated for each time interval. Via DRS the deposition of sulphide was monitored under the same conditions as used in the simulation (concentration / surface ratio). For each concentration of a certain aggregate, a correlation was searched for the different wavelength maximums in DRS. The results of the statistical analysis showed that a significant correlation could be found between the concentration of the monomer and the absorption at 505 nm, dimer and 560 nm, trimer and 620 nm. This calibration curve is represented in figure 5. From the optical data concerning the interaction of thiocyanate ions with incorporated gold ions also a correlation was found between the monomer and  $505 \text{ nm}^{10}$ .

A thorough optimization of the DRS sample preparation allowed the KM value (equation 1) to be linearly proportional to the concentration of the absorbing cluster entities. Since for all these experiments the composition, morphology and size of the silver halide crystals were identical, the scattering at each wavelength was constant:

$$KM_{\lambda,N} = \varepsilon'_{\lambda,N} C_N \quad (5)$$

The extinction coefficients and corresponding errors can be calculated from the slope of the different curves in figure 5.

$$\varepsilon'_{505 \text{ nm}, 1} = 333 \pm 29 \text{ mole Ag / mole (Ag}_2\text{S)}$$

$$\varepsilon'_{560 \text{ nm}, 2} = (1.7 \pm 0.2) \text{ E}3 \text{ mole Ag / mole (Ag}_2\text{S)}$$

$$\varepsilon'_{620 \text{ nm}, 3} = (9 \pm 3) \text{ E}3 \text{ mole Ag / mole (Ag}_2\text{S)}$$

Apparently, the extinction coefficient of large clusters is higher than that of smaller clusters. Other combinations of wavelengths and concentration of aggregates were investigated, but for none of these a linear fit could be found intercepting zero.

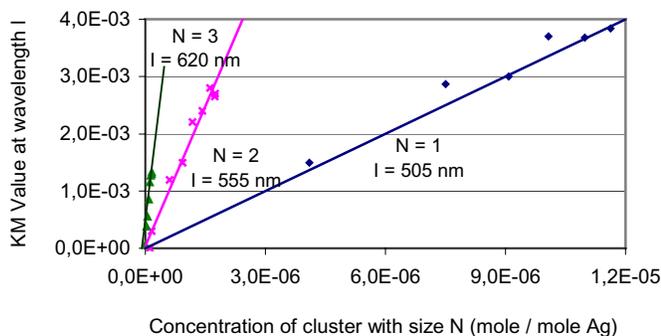


Figure 5. Calibration curves for clusters with different aggregation numbers at different wavelengths ( $2.0 \times 10^{-5}$  mole S / mole Ag,  $60^\circ\text{C}$ ,  $p\text{Ag}=7.36$ ,  $p\text{H}=4.20$ , reactive surface=1.0%)

## Conclusion

By measuring the uptake of gold ions into the silver sulphide clusters, it is possible to differentiate between monomers and multimers of silver sulphide. From a simulation we could derive that for a silver sulphide cluster with aggregation number  $N$ , a maximum of  $N-1$  gold ions can be incorporated into these clusters (assuming that gold is deposited on top of the clusters). Since this uptake of gold ions reaches a saturation level at a certain reaction time of sulphur a stable cluster distribution was formed, indicating that reacted sulphide entities have no mobility over the silver halide surface. Since there is no aggregation of sulphide, the silver sulphide cluster size distribution is completely determined by the random deposition of sulphide on the surface.

To simulate the deposition of silver sulphide clusters a computer program was written. By assuming a simple deposition model of sulphur on the surface, where all surface places are equal, a size distribution is obtained where the ratio of monomers / multimers is too high. From this simulated size distribution the gold uptake can be calculated and compared with the experimentally obtained values. To increase the number of multimers in our simulation, the number of reactive sites was decreased and catalysed deposition of sulphide by reacted sulphide was allowed. Our experimental data of the gold uptake could well be fitted in the used sulphur concentration range, assuming that only 1.0 % of the surface of our  $0.4 \mu\text{m}$  octahedral crystal was reactive. Under these conditions a size distribution is obtained where at optimal photographic sensitivity 785 dimers /  $\mu\text{m}^2$  are present per octahedral crystal of  $0.4 \mu\text{m}$ , but also larger cluster aggregates upto an aggregation number of 5. By using this simulation program a correlation could be found between the absorption values obtained via diffuse reflectance

spectroscopy of the monomer and 505 nm, the dimer at 555 nm and the trimer at 620 nm.

## References

- H. Kanzaki, Y. Tadakuma, Phys. Chem. Solids, 55, 631 (1994).
- J. Keevert, V. Gokhale, J. Imag. Sci., 31, 243 (1987).
- D. Sturmer, L. Blackburn, Paper F-4, SPSE 32nd Annual conference, Boston, (1979).
- D. Cash, J. Photogr. Sci. Eng., 29, 133 (1981).
- P. Roth, W. Simpson, Photogr. Sci. Eng., 24, 133 (1980).
- T. Tani, J. Imag. Sci. Technol., 42, 135 (1998).
- E. Charlier, M. Van Doorselaer, R. Gijbels, R. De Keyzer, I. Geuens, J. Imag. Sci. Technol., 44, 243 (2000).
- Y. Yoshida, H. Mifune, T. Tani, J. Soc. Photogr. Sci. Technol. Jp., 59, 541 (1996).
- T. Tani, Photographic Sensitivity, Theory and Mechanisms, Oxford University Press New York, pg. 165 (1995).
- E. Charlier, M. Van Doorselaer, R. De Keyzer, R. Gijbels, Functioning of thiocyanate ions during sulphur and sulphur-plus-gold sensitization, Proc. AgX 2000 (2000).
- M. Van Doorselaer, E. Charlier, A new approach to the mechanism of sulphur and sulphur + gold, Proc. ICPS Conference 98, pg. 267, (1998).
- E. Charlier, R. Gijbels, M. Van Doorselaer, R. De Keyzer, D. Vandenbroucke, I. Geuens, Role of silver interstitials in silver sulphide clusters formed during chemical sensitisation, Proc. ICPS Conference '98, pg. 455, (1998).
- G. Kortüm, Reflectance Spectroscopy, Springer Verlag, Berlin, pg. 106, (1969).
- W. Wendlandt, H. Hecht, Reflectance Spectroscopy, Interscience Publishers, New York, pg. 46, (1966).
- R. Hailstone, T. Zhao, Characterization of  $(\text{Ag}_2\text{S})_n$  clusters on AgBr grains, Proc. IS&T 49th Annual Conference, pg. 219, (1996).
- C. Lederer, S. Shirley, Table of the isotopes, 7th edition, John Wiley, New York, (1978).
- E. Moisar, J. Photogr. Sci., 20, 107, (1972).
- M. Fukui, Y. Hayashi, H. Yoshioka, J. Phys. Soc., 34, 1226, (1973).

## Acknowledgement

This work is partly supported by the Federal Services for Scientific, Technical and Cultural Affairs (DWTC/SSTC) of the Prime Minister's Office (contract nr. IUAP IV, P4/10).

## Biography

Evan Charlier received his Ph.D. in Chemistry at the University of Antwerp (Belgium) in early 2000, in close collaboration with Agfa-Gevaert N.V. The title of his thesis summarises nicely the main focus points of his research "Elucidating the structure and functioning of sulphide clusters grown epitaxially on the surface of AgBr microcrystals by using a combination of diffuse reflectance spectroscopy and tracer analysis".