

Growth and Characteristics of Liesegang Rings in Cu–Cr System: Optical and XRF Study

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Abstract. Liesegang rings were first discovered more than 100 years ago by German chemists R. E. Liesegang and they attracted much attention since then. Liesegang rings are observed as spontaneous evolution of precipitate ring structure during diffusion of certain electrolyte into medium containing other electrolyte. One such example is diffusion of CuSO_4 into gelatin containing K_2CrO_4 that is subject of our study. We present first results using X-Ray fluorescence technique for Cu–Cr system obtained at beam line BL4A, Photon Factory, KEK, Japan. Cu and Cr concentration profiles are in phase except the green ring at the boarder of the ring system with higher Cu concentration. Cu diffusion path is short, but in the case of 2 sources of CuSO_4 the diffusion path is enhanced between them due to interference. Conditions for ring growth and time evolution of the 2 sources experiment are described as well.

Introduction

Liesegang rings are important phenomenon in such different fields as chemistry, geology [*Liesegang*, 1945], biology [*Hein*, 1930], and medicine [*Tuur et al.*, 1987]. Liesegang rings are periodical rings or bands of precipitation first reported by R.E. Liesegang in 1896 [*Liesegang*, 1896]. They are formed spontaneously as a result of diffusion-reaction processes in various systems involving two electrolytes (which should produce precipitate) and supporting media (such as gelatin, agar-agar gel, silica gel and many others) [*Henisch*, 1988]. Inner electrolyte is immersed in the supporting media and outer electrolyte is poured onto it. Liesegang rings can be observed in three basic arrangements:

- test tubes–1D intersection of more complex shape, forms band of precipitate (Fig. 1, left),
- gel sheets–2D intersection of more complex shape, forms concentric rings of precipitate (Fig. 1, right),
- 3D structures–form concentric shells of precipitate.

In the test tube arrangement the gel is in test tube and outer electrolyte is poured onto it. In the gel sheet arrangement the gel is in the form of sheet and outer electrolyte is putted in form of droplet onto the surface. In 3D arrangement the outer electrolyte is putted into the gel block.

As nonlinear chemical system the Liesegang ring formation is dependent on many factors. The main factor is electrolyte concentrations because there exist concentration intervals in which the Liesegang rings are formed as rings, spirals or are not formed at all [*Hantz*, 2006]. Among other factors there are type and density of supporting media, light irradiation (some chemical systems need UV irradiation, others need darkness), temperature, acidity and presence/absence of other chemical compounds. The influence of these factors is not completely understood up today.

For better understanding of Liesegang rings formation mechanism it is useful to know distribution of particular chemical elements in the ring system. We used X-Ray fluorescence

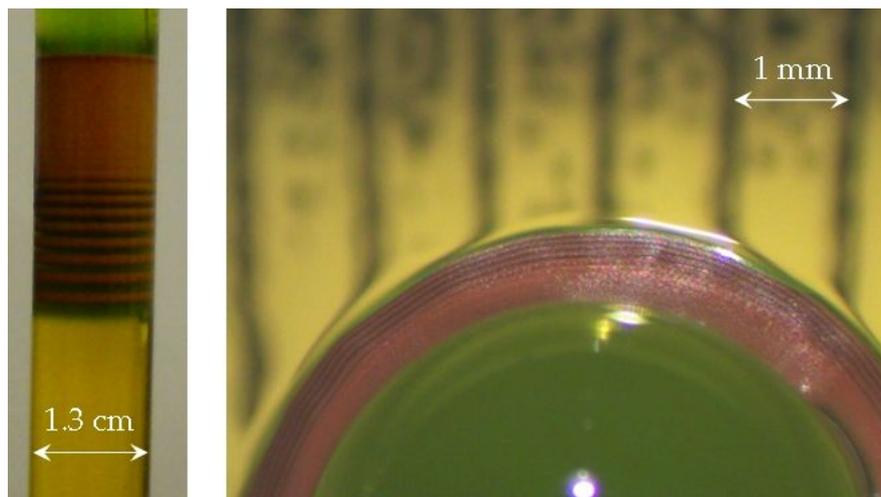


Figure 1. Liesegang rings in $\text{CuSO}_4 + \text{K}_2\text{CrO}_4$ system: test tube (left) and gel sheet (right) arrangements. Liesegang rings are horizontal bands in the case of test tube and red concentric rings in the gel sheet. Images are taken 169 hours after beginning of the experiment in the test tube and 169 minutes in the gel sheet case (for colored figures see electronic version [WDS]).

technique (XRF) for the mapping of the elements due to its nondestructivity. Our choice of $\text{CuSO}_4 + \text{K}_2\text{CrO}_4$ was given by the suitability of Cu and Cr for observation in our conditions. We didn't find any relevant literature about using XRF in Liesegang ring studies.

When two droplets are putted on the gel sheet some type of interference effect is observed. In the silver chromate system ($\text{AgNO}_3 + \text{K}_2\text{CrO}_4$) the rings formation is enhanced and sphere without precipitate is formed when the size differences between the droplets are big (these results will be published in another paper). In the case of copper chromate system ($\text{CuSO}_4 + \text{K}_2\text{CrO}_4$) the ring formation is suppressed between the droplets but copper diffusion is enhanced there as will be described further (the final shape is similar as in [Kuo, 1997]).

Sample preparation

One of Liesegang ring systems is $\text{CuSO}_4 + \text{K}_2\text{CrO}_4$ in gelatin. Essential ingredient for rings formation in this particular system is KH_2PO_4 , which probably serve for acidity stabilization [Das *et al.*, 1987]. We tried several electrolyte concentrations and for further experiments we used concentration that are summarized in Table 1.

Table 1. Electrolyte concentrations used in experiments.

Gel (inner electrolyte):	Outer electrolyte:
200 mM K_2CrO_4	1 M CuSO_4
25 mM KH_2PO_4	
5 % w/w gelatin	

Sample preparation procedure: 9 ml of distilled water was heated up to 85°C and continuously stirred. During heating 0.5 g of jelly powder (Maruha Nichiro, edible gelatine for cooking) was added and then 1 ml of 2M K_2CrO_4 and 34 mg of KH_2PO_4 were added (i.e. above-mentioned concentrations refer to solution without gelatin). Final solution was poured onto microscope glass (ca 1 ml per 2.5×2.5 cm glass substrate) and cooled down to 4°C in refrigerator.

As in the case of other Liesegang systems, sensitivity on inner electrolyte concentration is rather high (no rings at 250 mM K_2CrO_4), sensitivity on KH_2PO_4 wasn't tested but it is probably low (30 mM works as well, no rings without it), the same holds for gelatin concentration

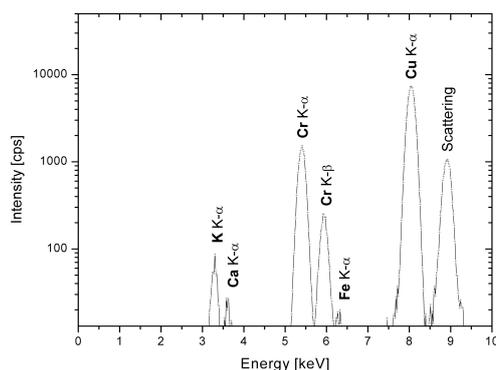


Figure 2. Typical XRF spectrum of Liesegang ring in $\text{CuSO}_4 + \text{K}_2\text{CrO}_4$ system. Calcium and iron are probably impurities from the substrate (microscope glass slide).

(it wasn't tested but the sensitivity is probably low, 7 % works as well). Sensitivity on outer electrolyte concentration is also low (tested for 0.7 M CuSO_4 and 1.3 M—which is upper limit of concentration because of CuSO_4 solubility). There were observed no substantial difference in ring formation with and without UV irradiation during experiment.

Concentration of K_2CrO_4 necessary for rings formation is about 40 times higher than in the case of more famous $\text{AgNO}_3\text{-K}_2\text{CrO}_4$ system (that is ca 5 mM K_2CrO_4). Such concentration influences gel stability and tends to K_2CrO_4 recrystallization during drying or even storage in the range of few days (in presence of outer electrolyte) up to a few weeks.

Rings are spatially limited to just a few rings in close vicinity of original droplet on the gel sheet. It consists of hard red precipitate with green layer on the edge. The structure is so compact that it can be extracted from the sample. Evolution takes a few hours during which the outer electrolyte in droplet is replaced by inner electrolyte due to diffusion. Large and regular structure is formed in test tube setting. The structure consists of red and green bands formed in about one week.

Measurement techniques

XRF data were taken at BL4A beamline in KEK Photon Factory, Japan, with beam energy of 9 keV, beam size of 25 μm , step of 25 μm and acquisition time of 50 s. BL4A beamline uses a bending magnet in the storage ring as a source of X-Rays. The X-Rays go through an XY slit to an Si(111) double crystals monochromator from which they go through another XY slit to a polycapillary optics, and finally reaching the sample. The focal depth is around 0.5 mm. The sample position is controlled by XYZ stage and in our case the Z direction was scanned. We used an Si(Li) detector which was placed several centimeters from the sample to avoid its saturation and to improve the signal/scattering ratio as well. We measured with multi-channel analyzer to obtain a full XRF spectra at each point for detailed study, hence quite long acquisition time.

Typical XRF spectrum is shown in Figure 2. It contains peaks from copper, chromium, potassium, calcium (from the glass substrate), iron (contaminant or glass substrate) and peak corresponding to scattered primary beam (merged with Cu K- β line). Concentration line profiles (e.g. Fig. 6) were obtained as an integral intensity of K- α lines of copper (7.81-8.26 keV), chromium (5.20-5.61 keV) and potassium (3.11-3.67 keV). Relation between XRF intensity of given element and its concentration is complicated. As we are not interested in absolute values of concentrations, rather in its relative values in different locations of the same sample, we can get by the well known fact that higher XRF intensity means higher concentration of studied element. Henceforward we will write about element concentrations based on XRF intensities and previously mentioned know relation.

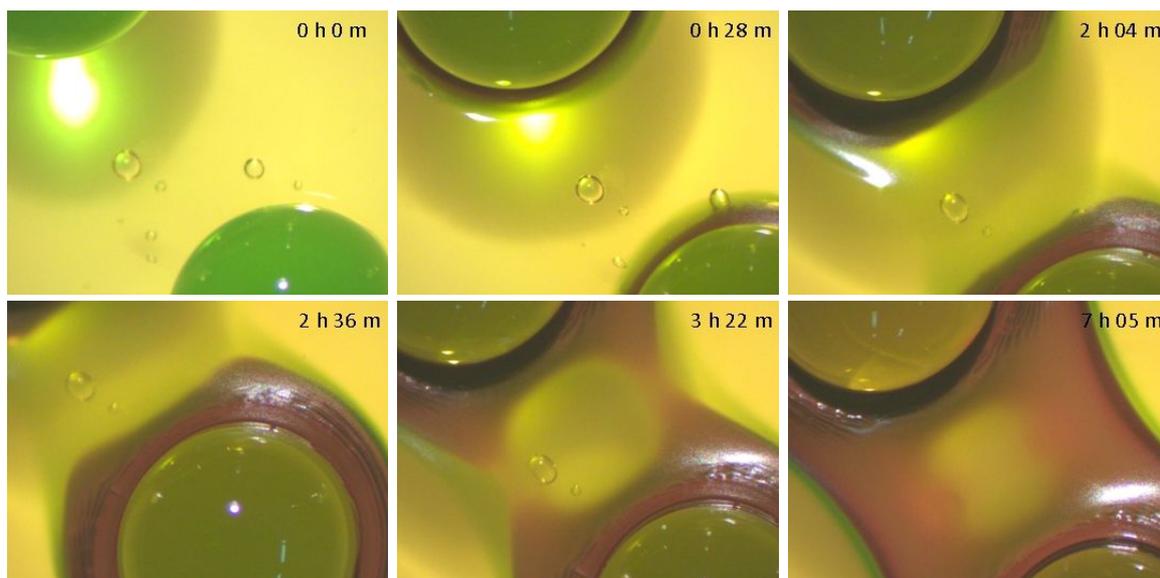


Figure 3. Temporal evolution of double droplet $\text{CuSO}_4 + \text{K}_2\text{CrO}_4$ experiment (gel: 5 % jelly powder, 2 M K_2CrO_4 and 25 mM KH_2PO_4 ; outer electrolyte: 0.7 M CuSO_4). Center-to-center distance of the droplets is 0.8 mm. For colored figures see electronic version [WDS].

It also should be mention that X–Rays make during scanning visible trace in the sample (not as good visible as in the case of silver chromate system but still visible). The trace shows evidences of slight photosensitivity of potassium chromate and the X–Ray beam intensity as well. The arisen trace can be used for visualizing the scanning path.

Results

First sample consisted of 2 M K_2CrO_4 and 25 mM KH_2PO_4 gel sheet with 2 holes in the center–to–center distance of about 8 mm. The holes were filled with 0.7 M CuSO_4 and the temporal evolution of this system is depicted in Fig. 3. Experiment was carried out at room temperature and ambient light illumination. Remaining liquid was removed from the holes before XRF measurement. Optical image of the sample before the measurement is depicted in Fig. 4 (left) and after the measurement Fig. 4 (right). Three scan paths are depicted in Fig. 4 as well. The sample was completely dry with clear traces of recrystallization after the measurement (that was running for about 12 hours).

Similarly, second sample consist of 2 M K_2CrO_4 and 25 mM KH_2PO_4 gel sheet with one hole filled with 1 M CuSO_4 . The CuSO_4 solution was replenished after 24 hours. After that a spit was formed on one side of originally circular structure. The spit is visible in Fig. 5 where you can see the scan path (LGD) as well. The spit has similar “ring” structure as it is expected for other Liesegang’s systems.

In Figures 6 and 7 there are magnified sections of scanned area (top) and concentration profile of copper, chromium and potassium (bottom). In LGA case the drop of concentration on the right side is due to hole in the gel made before the experiment. LGB scan has such holes on both sides and LGC on left side. Concentration profiles in the these areas are affected by remaining gel, substrate contaminants and remaining liquids and hence it is not very relevant for Liesegang phenomenon. It is worth to point out that copper signal is one order of magnitude stronger and potassium signal is one order of magnitude weaker than that of chromium.

In LGA XRF profile there is no apparent ring structure visible although the rings are observable in the optical image. The sharp drop of copper concentration in the outer region (left side) is noticeable (similar effect can be observed also on right side of LGC and LGD scans). It shows evidence of very limited diffusion path of copper. On the other hand there is no such sharp drop of copper concentration in LGB case, showing that copper diffusion is

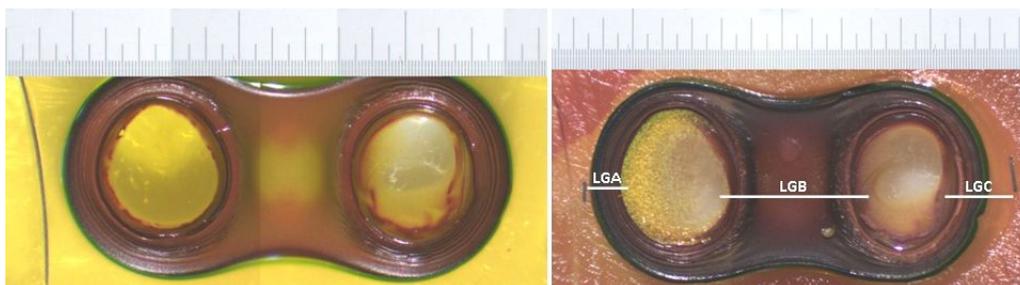


Figure 4. Sample from Fig. 3 before (left) and after (right) XRF measurement. Three XRF scans are shown in right image (LGA, LGB, LGC). For colored figures see electronic version [WDS].

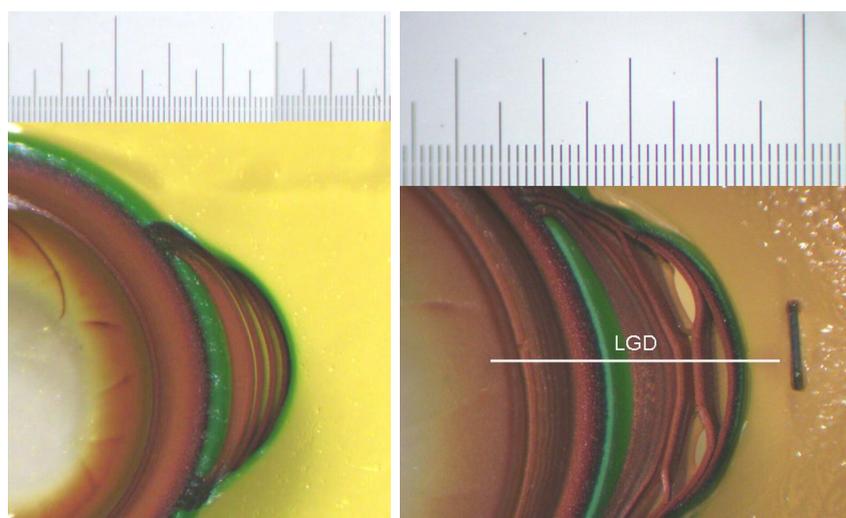


Figure 5. Sample 2 (gel: 5 % jelly powder, 2 M K_2CrO_4 and 25 mM KH_2PO_4 ; outer electrolyte: 1 M $CuSO_4$, replenished after 24 hours) before (left) and after (right) XRF measurement (major ticks: 1 mm). The XRF scan LGD is shown in right image (for colored figures see electronic version [WDS]).

enhanced between the droplets. LGC and especially LGD scans show several oscillations in concentration profiles corresponding to the ring structure. Although exact assignment of each ring to each oscillation is not easy, copper increase and diminution of chromium in the green ring is apparent. The XRF data also indicate that the maxima of copper (and chromium) concentrations correspond to the dark red rings and the minima to the orange (or light red) rings, respectively.

Discussion

Liesegang rings in Cu–Cr system consist of red and green bands which are best visible in the test tube arrangement. In the gel sheet arrangement the rings are usually very close (ca 100 μm) and separated by dark ring (green rings inside the inner rings region are not observed). In the outer region there is always green ring containing more copper and less chromium. Around the green ring there is an area with depleted chromium. The inner rings consist of dark red and orange rings. Whether the difference between them is chemical composition or structure is not known.

Problem of this Liesegang system is a structure of the precipitate which consist of hard rings with certain topology. Height of the precipitate is similar to original height of the gel (about 1 mm) and remain almost unchanged even after the gel is dried so the sample is not flat. Individual rings have slightly different height hence part of the oscillations in concentration

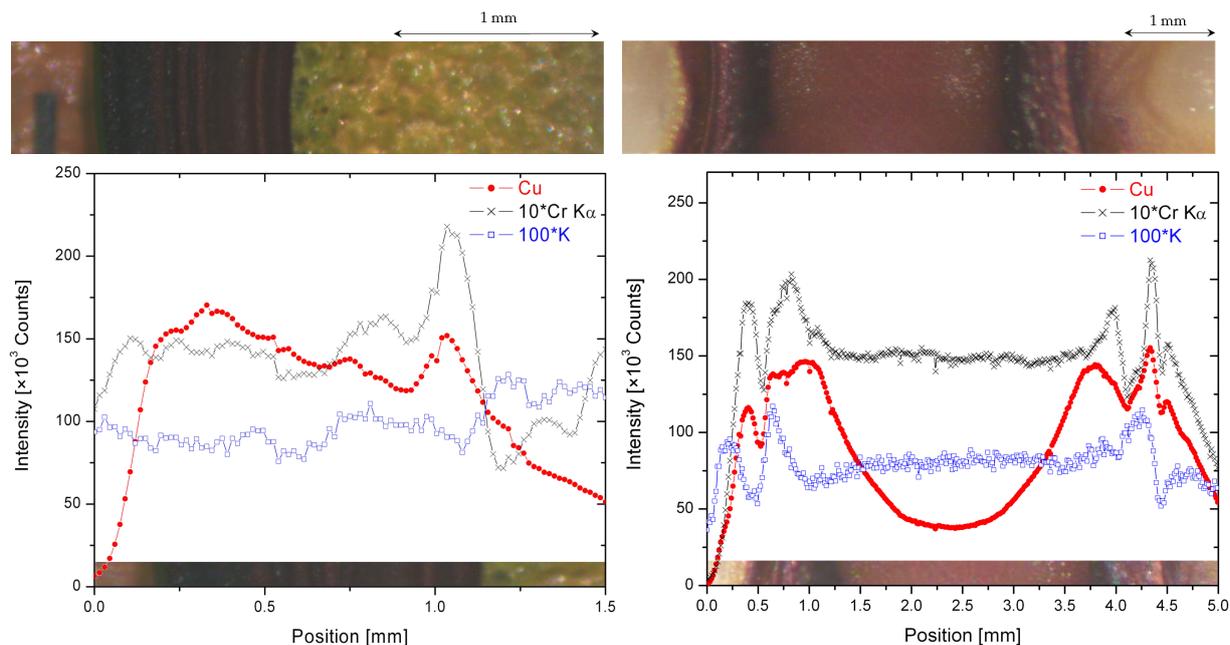


Figure 6. XRF scans: magnified section (top), concentration profile of copper (circles), chromium (crosses), and potassium (squares)—bottom, for LGA (left) and LGB (right) scans (sample from Fig. 4). For colored figures see electronic version [WDS]).

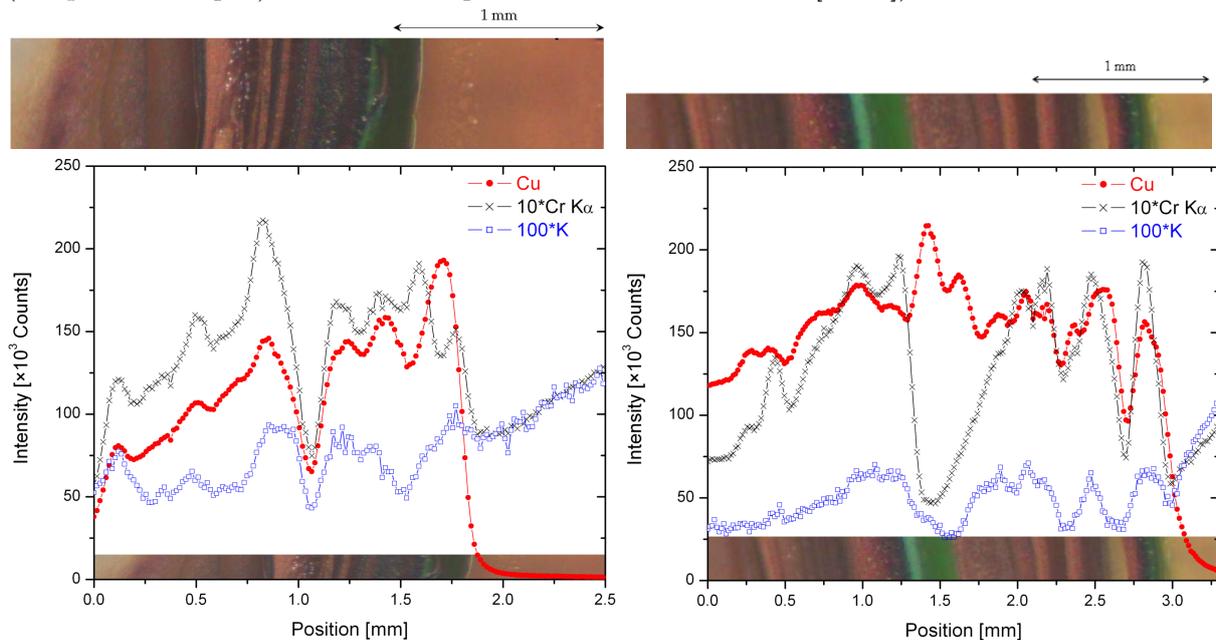


Figure 7. XRF scans: magnified section (top) and concentration profile of copper (circles), chromium (crosses), and potassium (squares)—bottom, for LGC (left) and LGD (right) scans (see Figs. 4 and 5, respective). For colored figures see electronic version [WDS]).

profiles could be caused by the height effect. These rings appear that they could be physically separated from each other under the microscope (enabling the chemical analysis of individual ring), but it has not been done (see Fig. 8). Such characteristics are completely different from that of $\text{AgNO}_3\text{-K}_2\text{CrO}_4$ system.

Oscillations of Cu and Cr concentrations are in phase except the green region on the edge (and green region in general) which has maximum of copper and minimum of Cr. It testify that the red rings are made of CuCrO_4 . Concentration profile of K is not as good as in the case



Figure 8. Extracted part of precipitate rings.

of Cu and Cr because of low XRF signal (due to low fluorescence efficiency) but it is almost in phase with Cu and Cr as well suggesting the conclusion that there exists rings produced by red precipitate and rings produced by other salt (K_2SO_4). Both ring structure are in the same locations. To confirm this conclusion the concentration profile of sulphur is needed but it can not be done in our experimental set-up. Also the role of phosphorus was not investigated. All scans show depletion of Cr behind the green ring, which is consistent with some theoretical expectation according to which the ring is formed from electrolyte afore and behind the ring hereby making depleted region around it [Stern, 1954].

Clearly observable in the first sample is the interference between outer electrolyte from the two droplets (Fig. 3). Red precipitate between the droplets is highly influenced and does not form full rings. In fact despite the Cu presence (green color) the precipitate formation is suppressed here probably due to faster diffusion causing lower Cu concentration.

Conclusion

We present concentration profiles of Cu, Cr and K in $CuSO_4-K_2CrO_4$ Liesegang ring system based on first XRF measurement known to us. The concentration line profiles depicted in Figs. 6 and 7 show that concentration profile of copper corresponds to the concentration profile of chromium except the green ring area usually situated on the edge of the structure which is rich in copper but depleted in chromium. The chemical analysis of particular rings is highly desired but it remains to be done. Diffusion of copper is spatially very limited to the close vicinity of the source and there is no copper behind the green ring.

Presence of second droplet (as the second source of Cu) disturbs the rings structure formation in between the droplets (see Fig. 3) as a result of interference. Although the diffusion ability of copper is enhanced in the direction between the droplets than in other directions (visible also in concentration line profiles in Fig. 6), the formation of the red precipitate is suppressed in the region between the droplets. Even when the precipitate is formed there is no ring structure in this region.

Finally, the $CuSO_4-K_2CrO_4$ system forms hard compact spatially limited precipitate structure that remains elevated high above the sample surface after drying and also the structure can be extracted from the sample. High concentration of K_2CrO_4 causes its recrystallization during drying and even during storage hence disturbing sample uniformity (another interesting feature is crystallization of various substances inside the precipitate structure during long term storage – after several weeks at room temperature large bluish and colorless crystals, small green bubbles, amber-like crystals and brown droplet-like structures were observed). From this point of view the $CuSO_4-K_2CrO_4$ system is not as suitable for XRF study of the ring growth process as e.g. $AgNO_3-K_2CrO_4$ system which have been also studied and will be published in different paper. However the copper diffusion enhancement in the two-droplets arrangement deserves further attention as well as the chemical composition of the particular rings.

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