

Cupric Chloride Crystallisation in the Presence of Additive: Experimental Conditions and Developmental Perspectives

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Zusammenfassung

Die Versuchsbedingungen der Kupferchlorid-Kristallisation-Methode mit Zusätzen wurden neu überarbeitet. Die neue Vorgehensweise hat die Homogenität der Kristallbilder und die Unterscheidungskraft der Methode verbessert. Ungeachtet der Reduktion der Streuung der Zeit bis zum ersten Kristallkeim (t_1) bleibt der Vorgang polarisiert. Es werden Verbesserungsmaßnahmen sowie technische Vereinfachungen vorgeschlagen, welche die Anwendbarkeit der Methode steigern können. Auch die Miniaturisierung der Methode würde zur Vereinfachung beitragen und könnte die Auswertung der Ergebnisse erleichtern.

Summary

The experimental conditions of the copperchloride crystallisation method in presence of additives was recently reviewed. A new operating procedure allowed improving the homogeneity of a crystallogram set as well as the discriminating power of the method. Notwithstanding reducing the spread of the appearance times of the first seed (t_1), the phenomenon is still polarised. Correctiv options are proposed as well as technical simplifications, which may improve the practicability of the method. Miniaturization of the method would also help to simplify its implementation and could facilitate the exploitation of results.

Résumé

Les conditions expérimentales de la méthode de cristallisation du chlorure cuivrique en présence d'additif ont été révisées récemment. Un nouveau mode opératoire a permis d'améliorer l'homogénéité des cristallogrammes d'une série et le pouvoir discriminant de la méthode. Nonobstant la réduction de la dispersion du temps d'apparition du premier germe de cristallisation (t_1), le phénomène de polarisation subsiste. Des hypothèses correctives sont proposées de même que des simplifications techniques permettant d'améliorer la praticabilité de la méthode. Sa miniaturisation contribuerait également à la simplification de sa mise en œuvre et pourrait faciliter l'exploitation des résultats.

Introduction

The crystallisation (nucleation and growth) of cupric chloride, S, from a thin film of an aqueous solution is partly modified by an additive, A, and partly by the surface tensions at the different interfaces of the system. Other factors relating to environmental and experimental conditions (temperature,

relative humidity, speed of evaporation, convection) can significantly influence the phenomenon, and consequently the appearance of the arborisation patterns formed. A very diverse range of chemical and biological substances, both soluble or insoluble, can affect the crystallisation of cupric chloride. Slight modifications or alterations of A are likely to significantly alter the arborisation structure.

These arborisations are produced when the growth takes place at a relatively high speed. Under these conditions the influence of A on crystallisation is inversely correlated with the driving force of crystallisation, i.e. the supersaturation (β) observed at the moment of appearance of the first crystal seed (*Reiter & Barth* 2010). Indeed, A enters into competition with S for the growth site; A generally slows crystallisation, promotes branching, but is not included in the crystal matrix.

Therefore, to ensure that comparative studies of crystallograms obtained with additives of the same nature are relevant, it is essential that the spread of the appearance times of the first seed, t_1 , is small.

Recent work (*Barth et al.* 2011; *Barth et al.* 2013) describes controlled experimental conditions that allow the reproducibility of the crystallograms to be improved. The progress made relates to the design and materials of construction of the crystallisation chamber, the control of climatic conditions, the wettability of the supports and the dilution of the mixtures to be crystallised. The results of these studies enable the definition of the general principles controlling the experimental conditions. Some improvements and new perspectives for application are briefly discussed.

Experimental details

Isotropy of the crystallisation chamber

Several laboratories (*Piva et al.* 1994; *Andersen et al.* 1998; *Fritz et al.* 2011; *Kahl* 2007) use rectangular or octagonal crystallisation chambers (CA). Most are made of wood, a material that has the disadvantage of varying in moisture content, a phenomenon which influences the external climatic conditions at any one time. The result is an experimental instability that is difficult to control, and adds to the uncertain airtightness of wooden walls. For all these reasons (geometry, wood, defective airtightness), the apparatuses cited do not allow the creation of an isotropic crystallisation environment.

On the other hand, the CA presented here is made of PVC, a hydrophobic plastic material which allows the creation of a watertight cylindrical space (o-rings, bath and drains filled with mineral oil). The crystallisation dishes are placed on a concentric annular table in the CA and exposed to