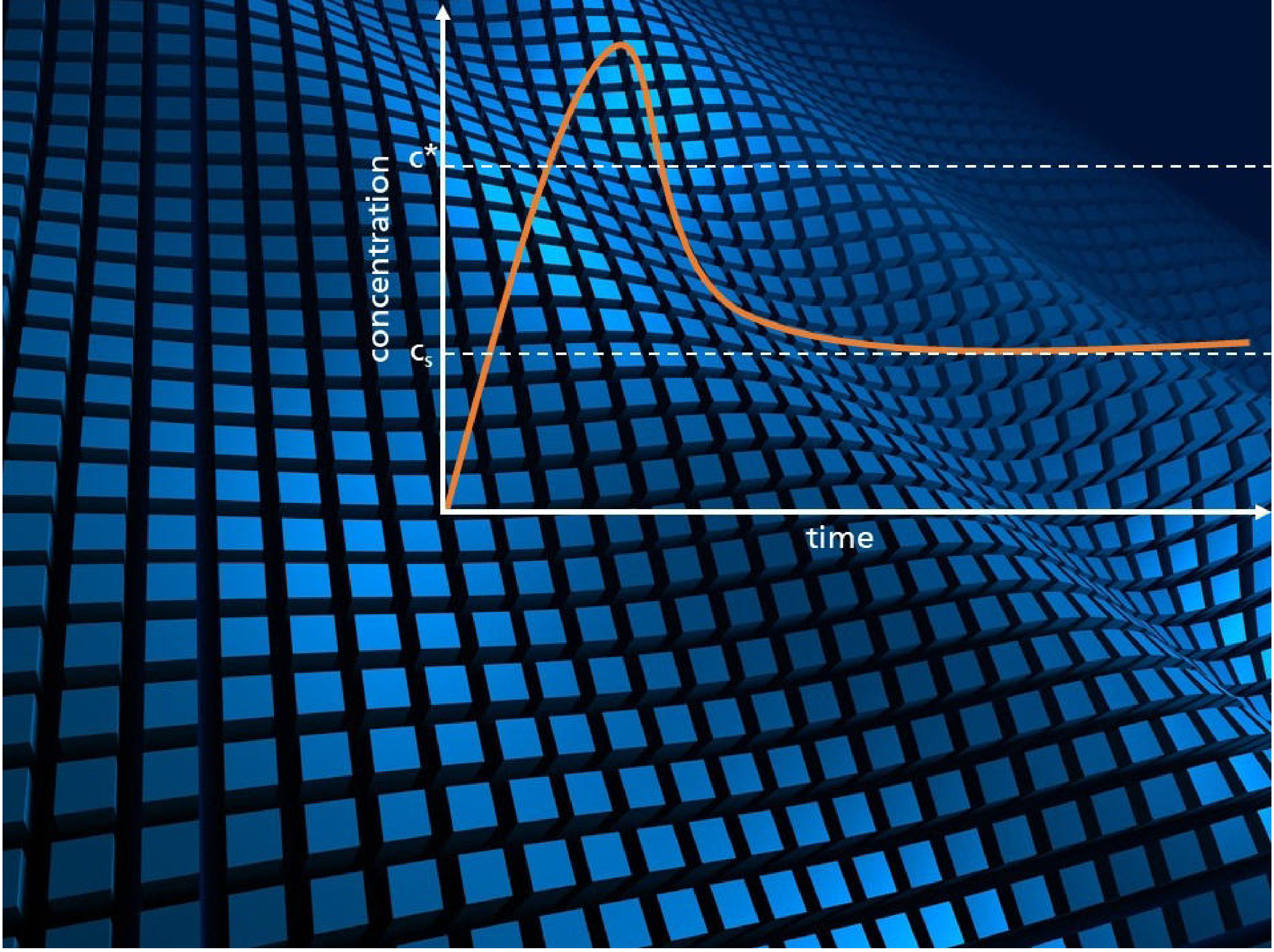

Application Note AN-I-034

Investigation of nucleation processes with automated titrators

Using ion-selective electrodes to monitor free ion activity in a precursor solution

Controlling the nucleation processes of a material can improve the quality of the final product and size distribution of its particles. As material properties can vary depending on the particle sizes (*cf.* quantum confinement), understanding and monitoring the formation process is beneficial for manufacturers. Using an automated titrator allows deeper insight into some of these events, helping to gain more control over a complex process which affects the properties of the finished material.

The monitored graph is related to the LaMer model, a kinetically controlled formation from a supersaturated precursor solution which undergoes nuclei formation. It is possible to monitor the solubility product, nucleation events, and crystal growth. Metrohm provides the required sensors and dosing components to investigate the ideal conditions for investigation, synthesis, and process control purposes. This Application Note covers the formation of calcium carbonate from solution.

SAMPLE AND SAMPLE PREPARATION

It is recommended to already have the solution and one component of the precursor prepared and to add the measured ion via a Metrohm dosing device. Sensor calibration and preconditioning depends on the system used for the investigation.

EXPERIMENTAL

Sensors and titrant solutions are used accordingly depending on the material and conditions to be investigated. As an example, the formation of calcium carbonate was examined. An OMNIS titrator was used in combination with OMNIS dosing modules (Figure 1) and a 902 Titrando. A carbonate solution was placed in a titration beaker and the pH was adjusted to 11 with a SET pH titration. After pH 11 was reached, a calcium chloride solution was added while the free Ca^{2+} concentration was measured in a MET U titration. Concurrently, a MEAS U with the Optrode was executed to monitor the qualitative transmittance of the solution. The pH of the solution was held at a static level with the STAT pH command executed via the 902 Titrando. For screening and optimizing parameters, a sample robot can be applied to increase sample throughput.

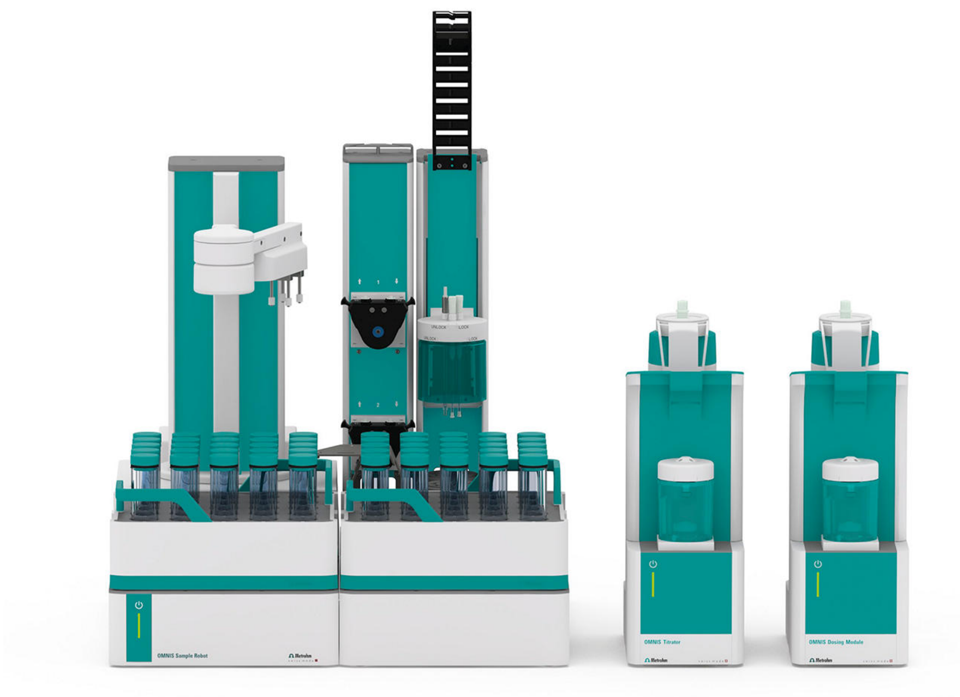

Figure 1. OMNIS Titrator with an OMNIS Dosing Module and an OMNIS sample robot S.

The observation of calcium carbonate formation is shown in Figure 2. At the beginning, the potential without any calcium ions is displayed. Calcium is added at defined intervals into the carbonate-containing solution while the Ca^{2+} ion potential is monitored. The obtained U/t resp. U/V curve is related to the LaMer diagram with its different stages. At the beginning, an undersaturated solution is present without any solid phase formed (I). The potential increases due to added calcium ions, continuing to increase until nucleation takes place (II) and $CaCO_3$ forms. The transmittance (shown in orange) decreases dramatically once enough stable particles are formed. After the formation of stable particles, the calcium ion concentration in the solution decreases due to particle growth (III) and settles into a potential plateau. The potential at the plateau corresponds to a defined calcium ion concentration. This concentration equals the solubility product of $CaCO_3$ at the defined reaction conditions.

RESULTS

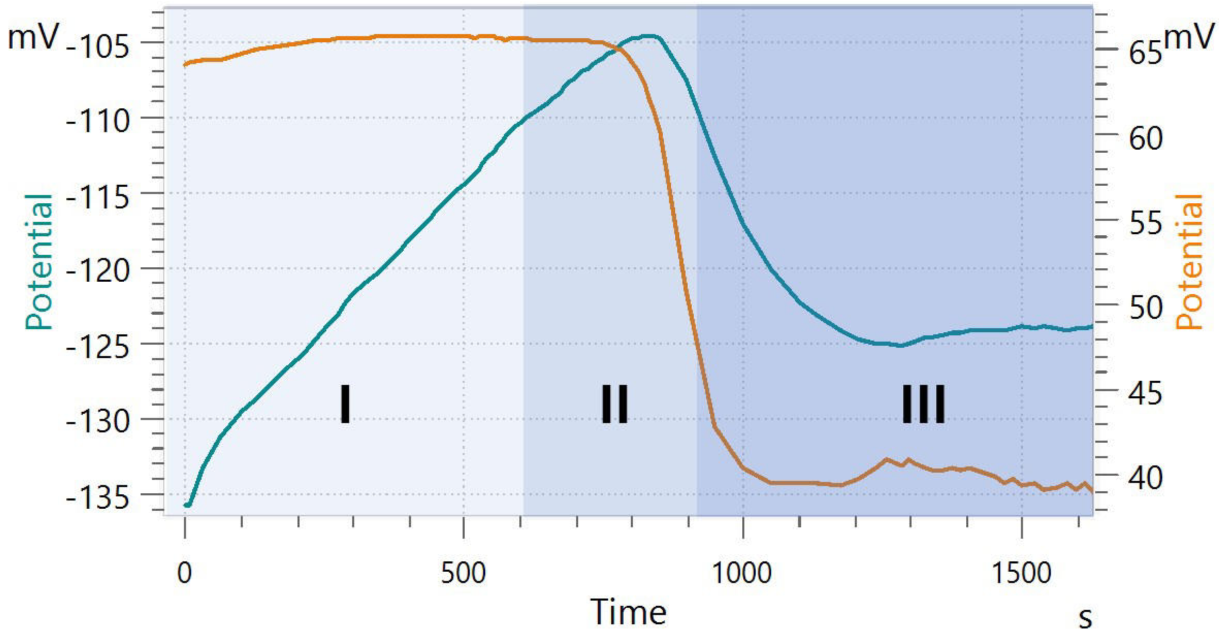

Figure 2. Example curve for calcium carbonate formation. In green is the potential of the free calcium ions measured with the combined Ca ion-selective electrode, and in orange, the potential measured with the Optrode. The experiment was carried out at pH 11. The colored phases describe the prenucleation phase (I), nucleation (II), and particle growth (III).

Both curves, calcium potential and transmittance potential, can be fused together with the COLLECT command and can be displayed in one graph.

Metrohm instruments provide superior performance for investigation of nucleation processes in various fields (e.g., materials science, biomineralization, pharmaceuticals, and geology). Different ion-selective electrodes can be applied including calcium, lead, copper, and much more.

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