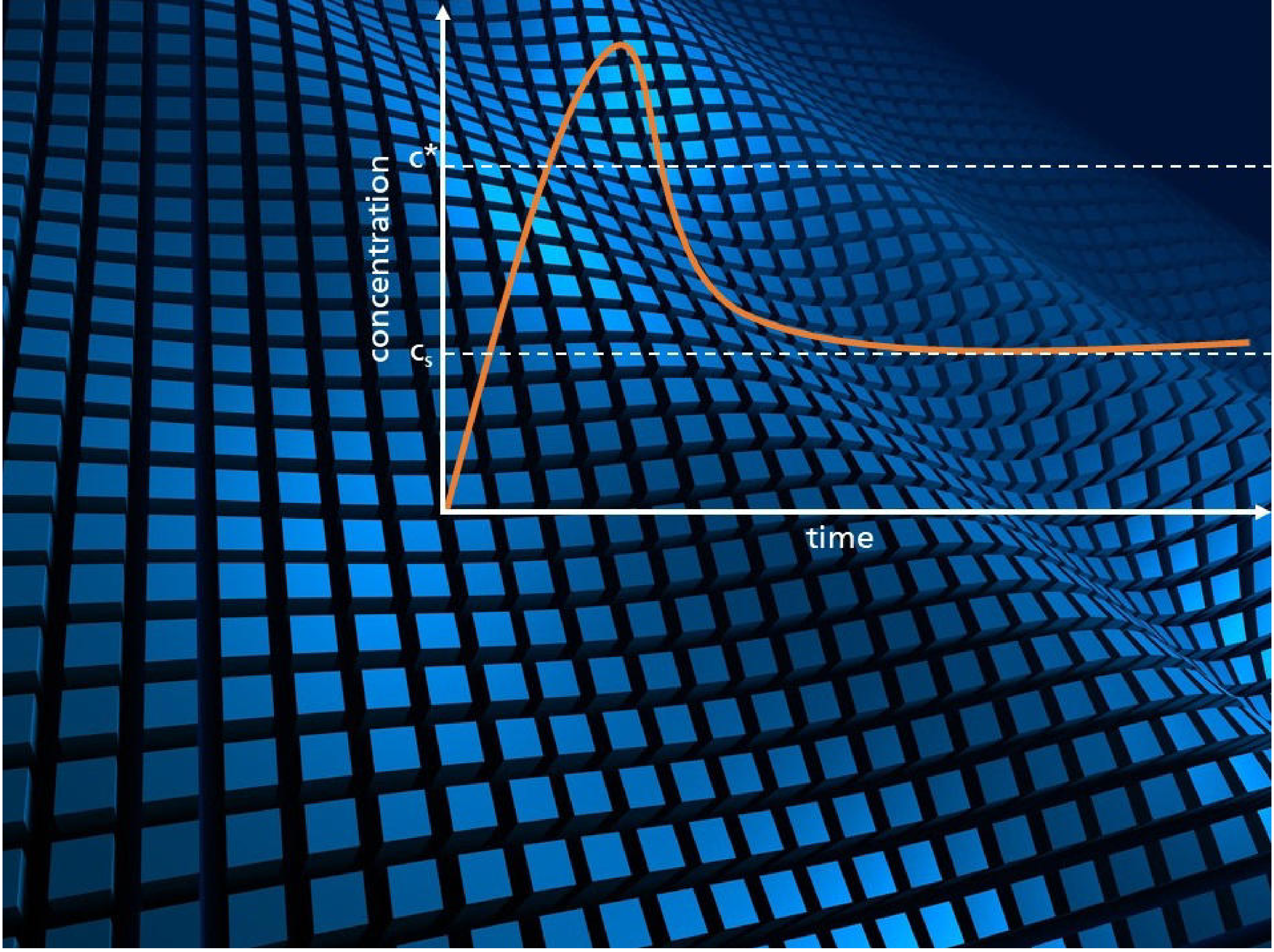

Application Note AN-I-034

用自动滴定仪研究成核过程

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.

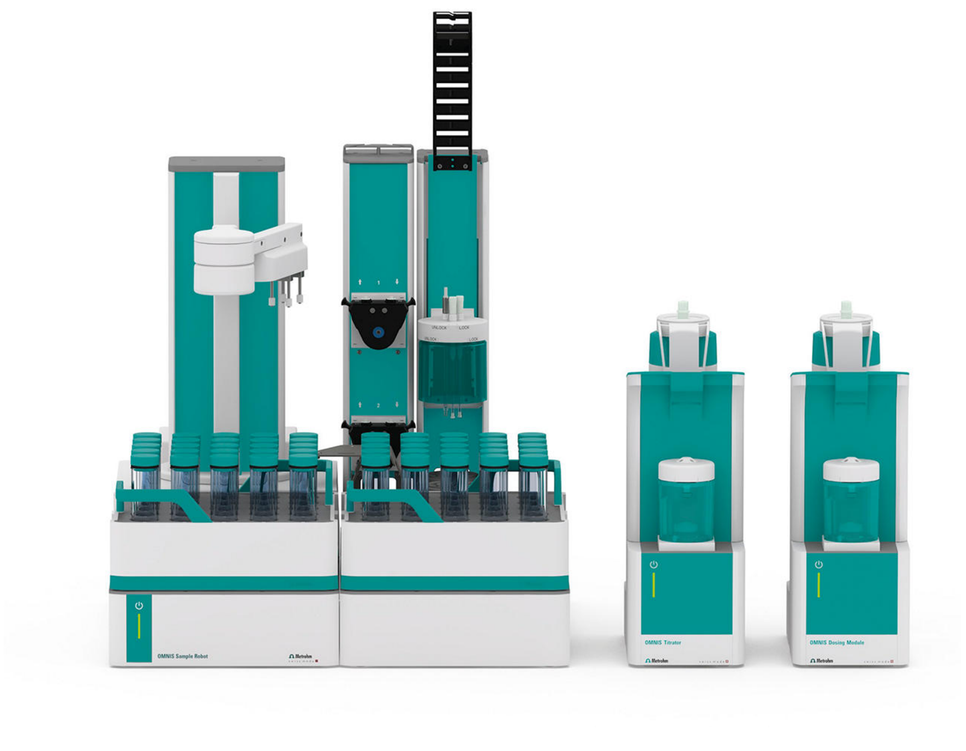

Figure 1. OMNIS Titrator with an OMNIS Dosing Module and an OMNIS sample robot S.

RESULTS

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.

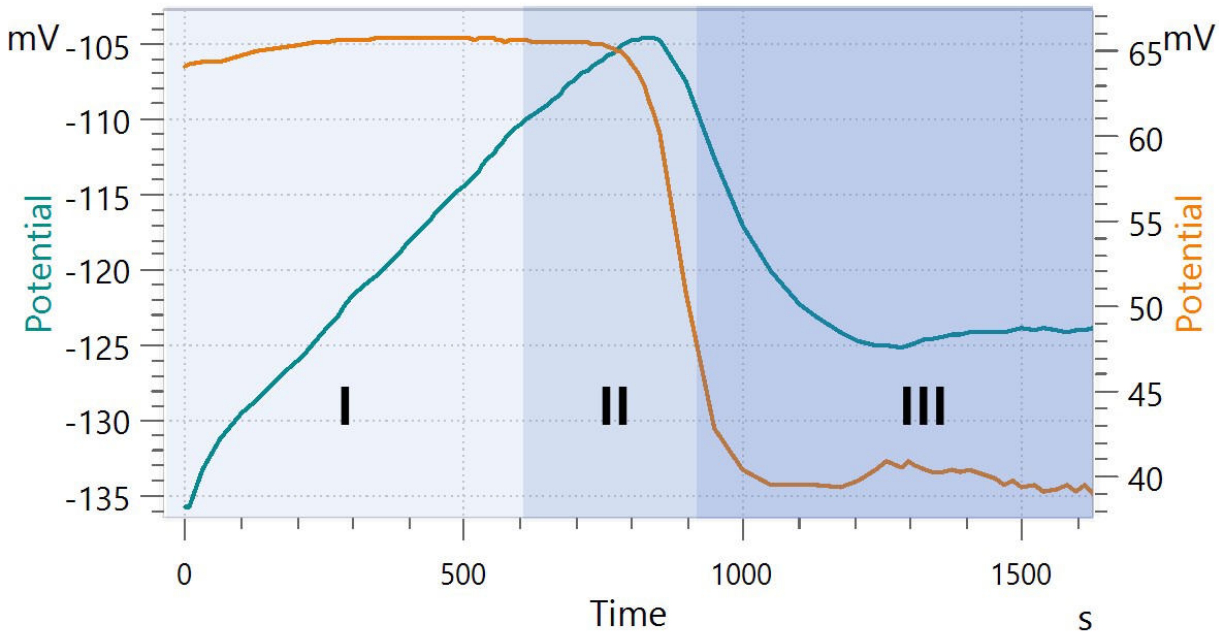

Figure 2. Example curve for calcium carbonate formation. In green is the potential of the free calcium ions measured with the combined Ca ion-selective electrode, and in orange, the potential measured with the Optrode. The experiment was carried out at pH 11. The colored phases describe the prenucleation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

CONCLUSION

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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CONFIGURATION

907 Titrando

用于使用两个测量接口和 Dosino 加液单元电位分析和容量卡尔·费休滴定法滴定的电位滴定仪。

- 多达四套 800 Dosino 加液系统
- 动态(DET)、等量(MET)和终点滴定(SET),酶和 pH-STAT 滴定(STAT)、卡尔·费休容量滴定 (KFT)
- 智能电极“iTrode”
- 使用离子选择性电极测量(MEAS CONC)
- 带监控的加液功能,LQH
- 用于其他搅拌器或加液器系统的四个 MSB 接口
- USB 接口
- 使用 OMNIS-Software、*tiamo*-软件或 Touch Control
- 如果需要,满足 GMP/GLP 和 FDA 要求,比如 21 CFR 第 11 部分

906 Titrando

用于使用 2 个测量接口和内部加液器驱动电位分析滴定和容量卡尔·费休滴定法滴定的高端滴定仪。

- 内置的加液器驱动
- 动态(DET)、等量(MET)和终点设定滴定(SET),酶和 pH-STAT 滴定(STAT)、卡尔·费休滴定法(KFT)
- 使用离子选择性电极测量(MEAS CONC)
- 带监控的加液功能,灵快量化液体处理
- 4 个 MSB 接口
- **2 个电流分隔的测量接口**
- USB 接口
- 使用 OMNIS-Software、*tiamo* 软件或 Touch Control
- 如果需要,满足 GMP/GLP 和 FDA 要求,比如 21 CFR 第 11 部分

902 Titrando

用于通过一个测量接口终点设定滴定(SET)及酶和 pH-STAT 滴定(STAT)的电位滴定仪。

- 多达四套 800 Dosino 加液系统
- 带监控的加液功能,LQH 和串联加液
- 用于额外搅拌器或加液器系统的四个 MSB 接口
- 可以扩展额外的测量接口
- USB 接口
- 使用 OMNIS-Software、*tiamo*-软件或 Touch Control
- 如果需要,满足 GMP/GLP 和 FDA 要求,比如 21 CFR 第 11 部分

OMNIS Titrator

创新型、模块式电位分析 OMNIS Titrator 滴定仪,适于独立运行或作为 OMNIS 滴定系统的核心元件运行。由于采用 3S 试剂瓶适配器技术,处理化学品很安全。可以使用测量模块和计量管单元自由配置滴定仪,并在需要时扩展一台搅拌器。由于采用不同的软件功能许可证,因此可以有不同的测量模式和功能。

- 通过计算机或本地网络控制
- 可以为其他应用或辅助溶液另外连接四个滴定模块或加液模块
- 螺旋搅拌器的连接方式
- 可提供不同大小的计量管:5、10、20 或 50 mL
- 采用 3S 技术的试剂瓶适配器:安全处理化学品,自动传输生产商的原始试剂数据

测量模式和软件选项:

- 终点设定滴定:“Basic” 功能许可证
- 终点和等当点滴定(单一/动态):“Advanced” 功能许可证
- 终点和等当点滴定(单一/动态),包括平行滴定:“Professional” 功能许可证

dCa-ISE

用于 OMNIS 的数字、组合式钙选择性电极。
该 ISE 电极适用于:

- 水性溶液中 Ca2+ 的离子滴定(1*10-7 至 1 mol/L)
- 络合滴定(复)滴定(例如:测定水硬度)

得益于坚固/为易碎的聚丙烯塑料杆和高分子膜片衬垫,传感器可以承受较高的机械载荷。
作为参比电机,我们使用了 c(KCl) = 3 mol/L。
dTrodes 可在 OMNIS Titratoren 上使用。

Pb

具有晶体膜的铅选择性电极。
这种 ISE 必须搭配参比电极使用,并且适用于:

- Pb2+ 的离子测量(10-6 至 0.1 mol/L)
- 小样品体积的离子测量(最小浸没深度为 1 mm)
- 滴定(例如:用硝酸铅测定硫酸盐)

得益于 EP 材质的坚固/不易破碎的塑料杆,该传感器可以承受较高的机械载荷。
使用随供的抛光套件,可以轻松清洁和更新电极表面。

Unitrode

用于 pH 滴定的组合 pH 电极。它特别适用于:

- 在较难的、粘性或碱性样品中进行 pH 滴定
- 温度升高的时候

固定磨口隔膜对污染不敏感。

参比电极:c(KCl) = 3 mol / L,储存在储存溶剂中。
替代方法:T>80° C 时的滴定用参比电解质,储存在 Idrolyt 中。