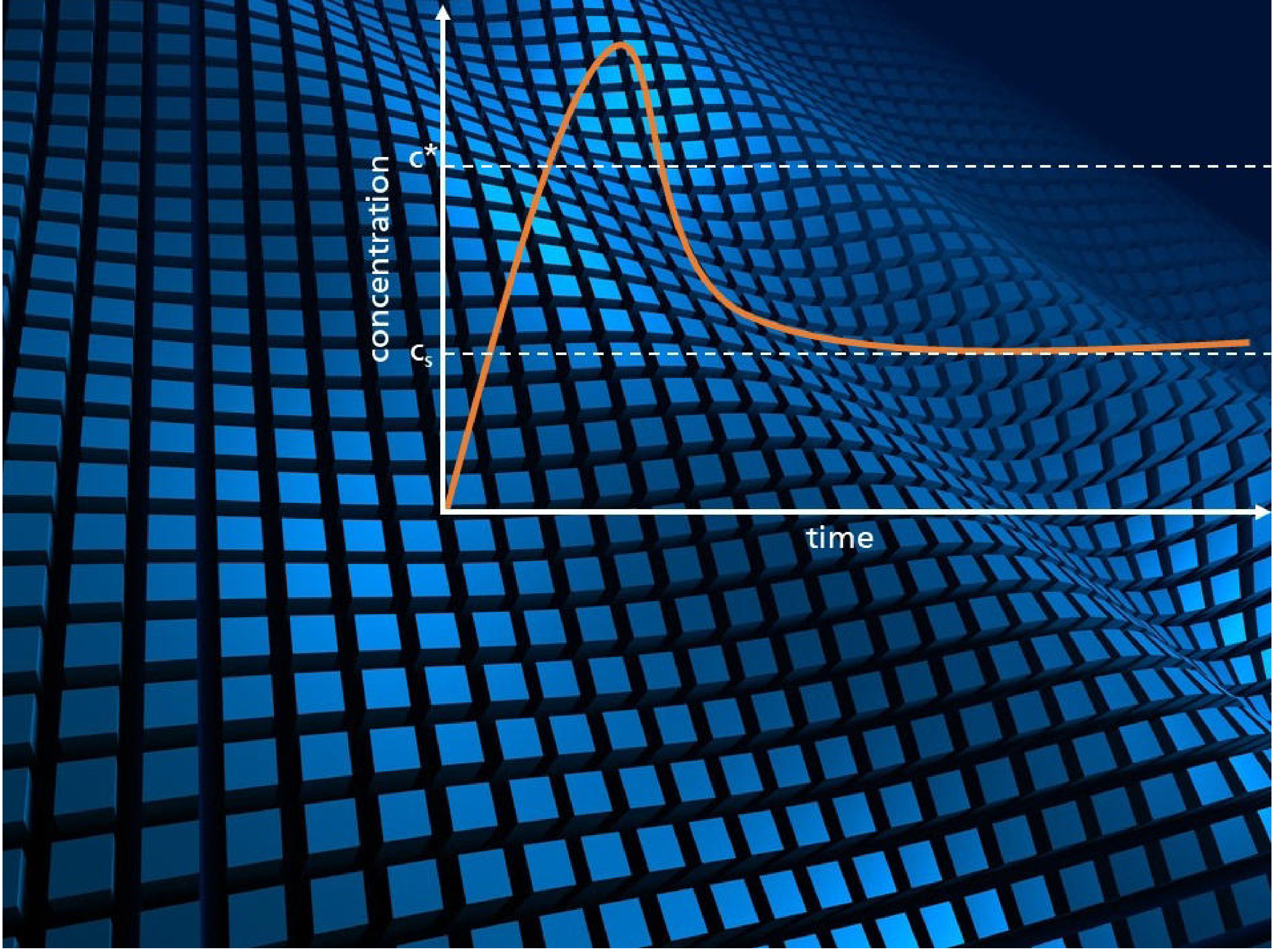

Application Note AN-I-034

用自滴定研究成核程

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.

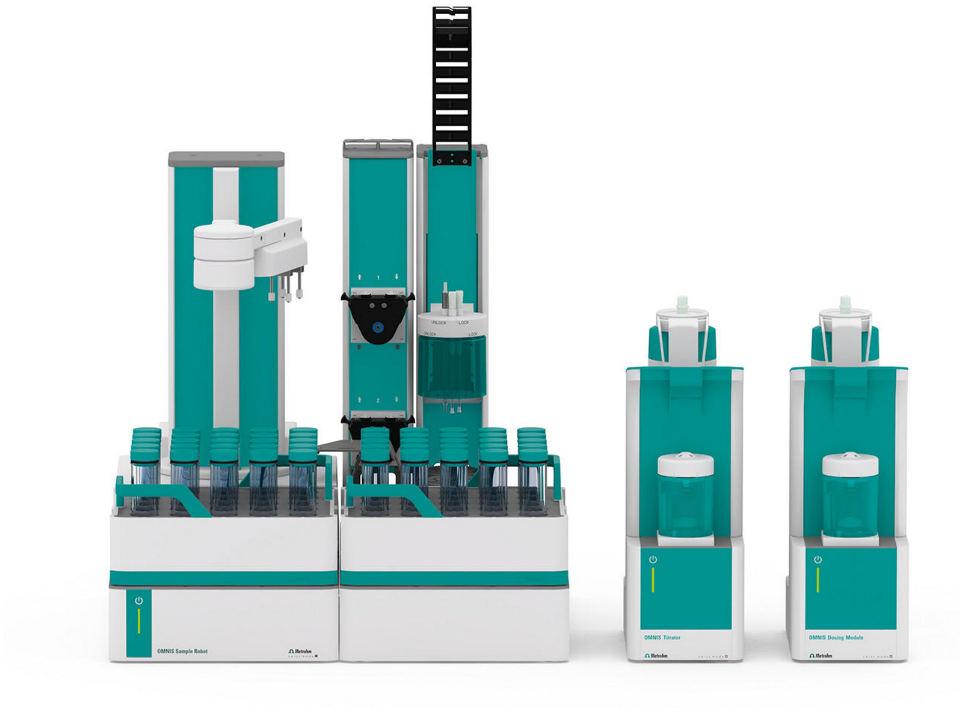

Figure 1. OMNIS Titrator with an OMNIS Dosing Module and an OMNIS sample robot S.

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.

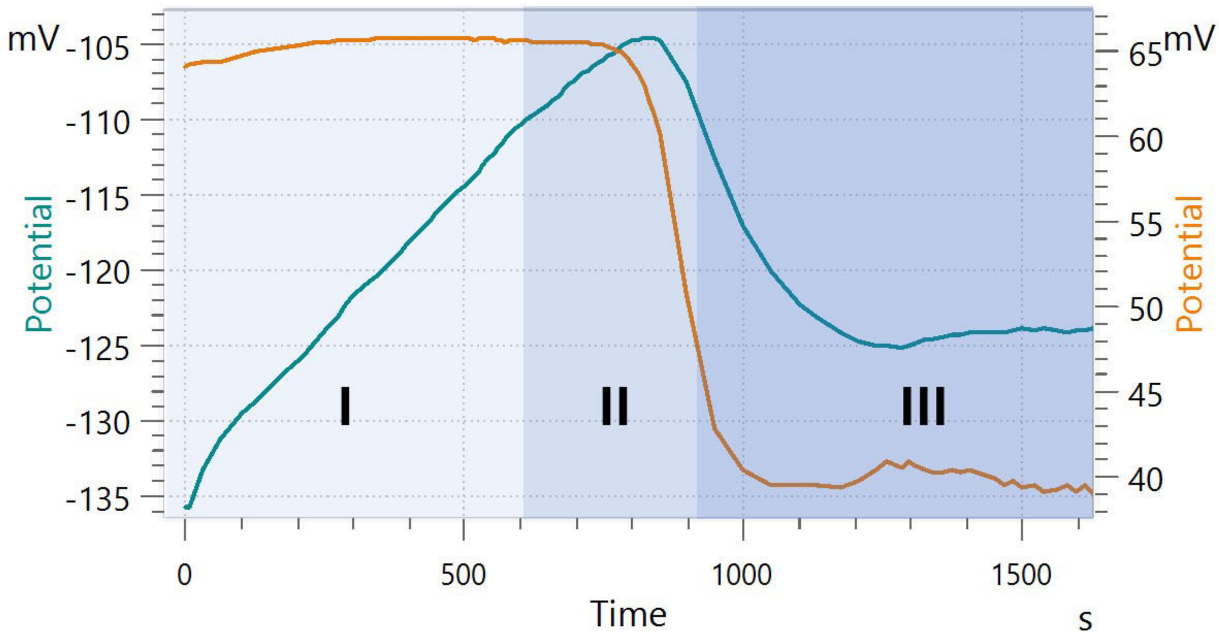

Figure 2. Example curve for calcium carbonate formation. In green is the potential of the free calcium ions measured with the combined Ca ion-selective electrode, and in orange, the potential measured with the Optrode. The experiment was carried out at pH 11. The colored phases describe the prenucleation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

CONTACT

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CONFIGURATION

907 Titrando
用于使用个量接口和 Dosino 加液元位分析和容量·休滴定法滴定的位滴定。

- 多四套 800 Dosino 加液系
- (DET)、等量(MET)和点滴定(SET),和 pH-STAT 滴定(STAT)、·休容量滴定(KFT)
- 智能“iTrode”
- 使用子性量(MEAS CONC)
- 控的加液功能,LQH
- 用于其他拌器或加液器系的四个 MSB 接口
- USB 接口
- 使用 OMNIS-Software、*tiamo*-件或 Touch Control
- 如果需要,足 GMP/GLP 和 FDA 要求,比如 21 CFR 第 11 部分

906 Titrando

用于使用 2 个量接口和内部加液器位分析滴定和容量·休滴定法滴定的高端滴定。

- 内置的加液器
- (DET)、等量(MET)和点定滴定(SET),和 pH-STAT 滴定(STAT)、·休滴定法(KFT)
- 使用子性量(MEAS CONC)
- 控的加液功能,快量化液体理
- 4 个 MSB 接口
- **2 个流分隔的量接口**
- USB 接口
- 使用 OMNIS-Software、*tiamo* 件或 Touch Control
- 如果需要,足 GMP/GLP 和 FDA 要求,比如 21 CFR 第 11 部分

902 Titrando

用于通一个量接口点定滴定(SET)及和 pH-STAT 滴定(STAT)的位滴定。

- 多四套 800 Dosino 加液系
- 控的加液功能,LQH 和串加液
- 用于外拌器或加液器系的四个 MSB 接口
- 可以展外的量接口
- USB 接口
- 使用 OMNIS-Software、*tiamo*-件或 Touch Control
- 如果需要,足 GMP/GLP 和 FDA 要求,比如 21 CFR 第 11 部分

OMNIS Titrator

新型、模式位分析 OMNIS Titrator 滴定,于独立行或作 OMNIS 滴定系的核心元件行。由于采用 3S 瓶配器技,理化学品很安全。可以使用量模和量管元自由配置滴定,并在需要展一台拌器。由于采用不同的件功能可,因此可以有不同的量模式和功能。

- 通算机或本地网控制
- 可以其他用或助溶液外接四个滴定模或加液模
- 螺旋拌器的接方式
- 可提供不同大小的量管:5、10、20 或 50 mL
- 采用 3S 技的瓶配器:安全理化学品,自生商的原始数据

量模式和件:

- 点定滴定:“Basic” 功能可
- 点和等当点滴定(一/):“Advanced” 功能可
- 点和等当点滴定(一/),包括平行滴定:“Professional” 功能可

dCa-ISE

用于 OMNIS 的数字、合式性。

ISE 用于:

- 水性溶液中 Ca^{2+} 的子滴定(1*10-7 至 1 mol/L)
- 合滴定()滴定(例如:定水硬度)

得益于固/易碎的聚丙塑料杆和高分子膜片,感器可以承受高的机械荷。

作参比机,我使用了 c(KCl) = 3 mol/L。

dTrodes 可在 OMNIS Titratoren 上使用。

Pb

具有晶体膜的性。

ISE 必搭配参比使用,并且用于:

- Pb^{2+} 的子量(10-6 至 0.1 mol/L)
- 小品体的子量(最小浸没深度 1 mm)
- 滴定(例如:用硝酸定硫酸)

得益于 EP 材的固/不易破碎的塑料杆,感器可以承受高的机械荷。

使用随供的抛光套件,可以松清和更新表面。

Unitrode

用于 pH 滴定的合 pH 。它特用于:

- 在的、粘性或性品中行 pH 滴定
- 温度升高的候

固定磨口隔膜染不敏感。

参比:c(KCl) = 3 mol / L,存在存溶中。

替代方法:T>80° C 的滴定用参比解,存在 Idrolyt 中
。