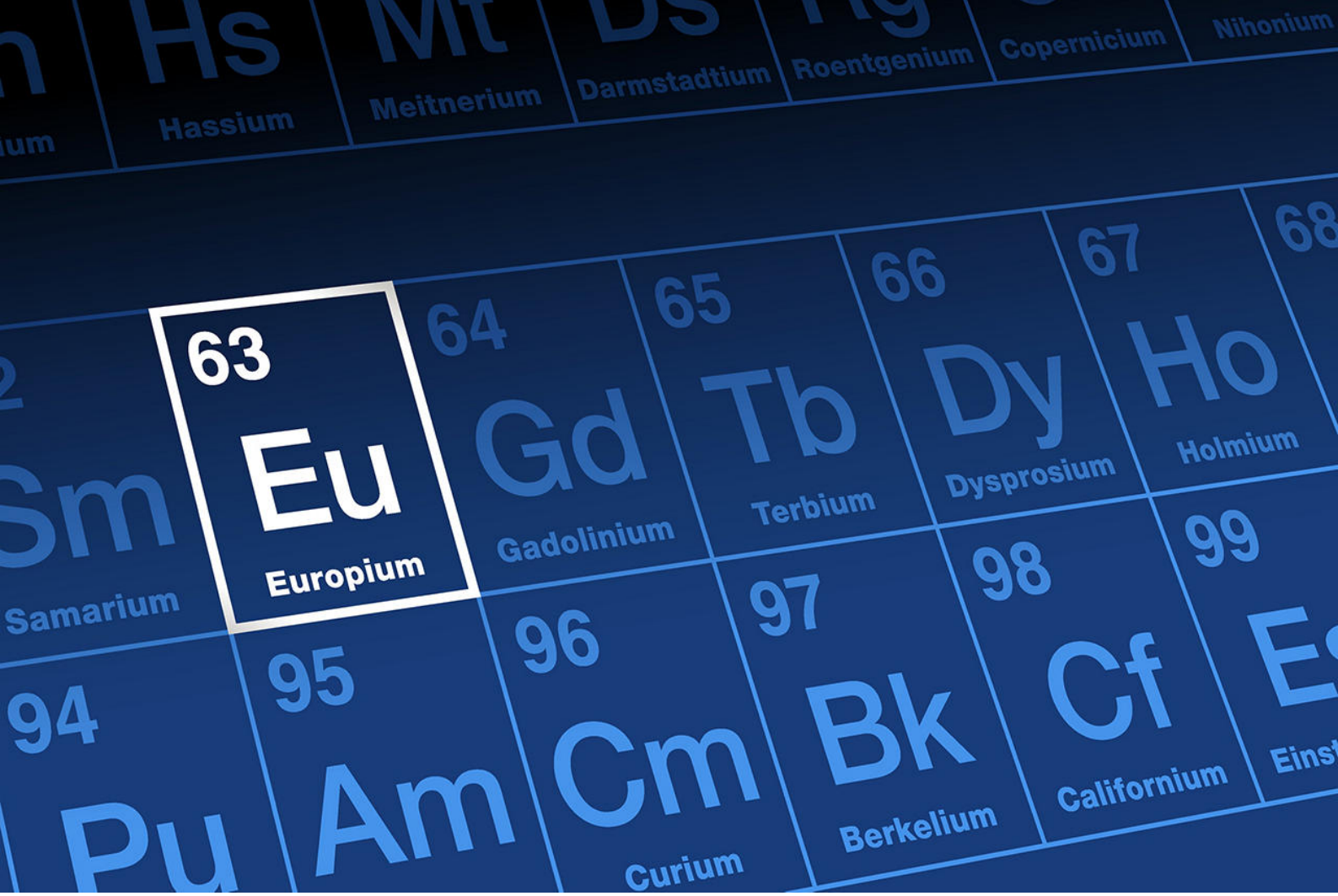

Application Note AN-T-250

稀土元素 (REEs)电位分析法

Accurate and precise back-titration of rare earth elements with the copper-selective electrode

Rare earth metals are comprised of 17 elements including the lanthanide series as well as the elements scandium and yttrium. These REEs are primarily used in batteries, nanotechnology, photovoltaics, medical technology, aerospace, and military technology.

The concentrations of REEs in ore and rock must be measured to determine the viability of a rare earth deposit. After crushing, the ores are dissolved, separated, and purified, and the REEs, along with other elements, are monitored throughout this stage. Determining the mass fraction of rare earth metals here is crucial and involves significant effort.

This Application Note presents a rapid and precise back-titration method using the Cu-ISE, which clearly separates a number of rare earth metals, even when they are combined with other elements, and enables them to be analyzed with nearly 100% recovery.

INTRODUCTION

Alongside gravimetry, rare earth metals titration is an absolute method which is often used as a reference for chromatographic and spectroscopic methods. As sample preparation for titration and ICP (inductively coupled plasma) is virtually identical, titration offers unbeatable cost and effort advantages in this case. Furthermore, back-titration is highly flexible and can be adapted to individual customer samples. Titration can therefore certainly be used as a rapid on-site analytical method.

A standardized ethylenediaminetetraacetic acid (EDTA) solution is added in excess to the dissolved and buffered rare earth sample (Ln^{3+}). An EDTA-metal complex then forms. Any unused EDTA is then back-titrated with copper sulfate.

The following reactions offer a highly simplified description of the titration:

$Ln^{3+} + EDTA \rightarrow Ln(EDTA)$

$CuSO_4 + EDTA_{(excess)} \rightarrow Cu(EDTA)$

The amount of rare earth content can be calculated based on the amount of copper sulfate used.

SAMPLE AND SAMPLE PREPARATION

This application is demonstrated on yttrium, scandium, lanthanum, cerium, and neodymium standard solutions. In addition, testing was performed on a mixture of lanthanum and scandium, as well as a synthetic mineral sample that closely resembles steenstrupine.

No sample preparation is required.

EXPERIMENTAL

The determination is carried out using an OMNIS Sample Robot S – WSM, an OMNIS Professional Titrator equipped with OMNIS Dosing Modules, as well as a copper-selective electrode (Figure 1).

An appropriate amount of sample is weighed into the titration beaker, and acetate buffer as well as standardized EDTA solution are added. After a waiting time, the solution is titrated until after the first or second equivalence point with standardized $CuSO_4$ solution.

Figure 1. OMNIS Sample Robot S – WSM equipped with an OMNIS Titrator, dosing modules, and copper-selective electrode for the automated determination of rare earth samples.

RESULTS

As shown in **Table 1**, the results for the REE standards present high recovery rates and confirm the robustness of the back-titration.

Table 2 shows the results for the lanthanum and scandium sample mixture. This demonstrates the potential for separating the two rare earth elements, with good recovery rates for both.

The result of the synthetically made REE mineral «steenstrupine» with a mass concentration of 8.000 g/L of cerium and an approximate molecular composition of $Na_{7.9}H_XCe_6Mn_{1.6}Fe_{1.8}Zr_{0.3}P_{4.5}Si_{1.7}Cl_{4.4}N_{7.9}S_6O_Y$ is summarized in **Table 3**.

An exemplary titration curve of a mixture of lanthanum and scandium is given in **Figure 2**.

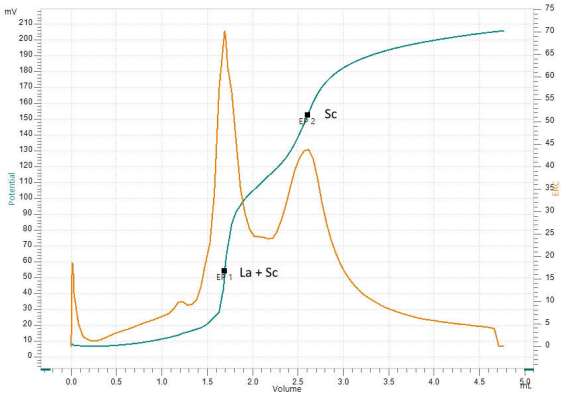

Figure 2. Back-titration of a mixture of lanthanum and scandium with the Cu-ISE. EP1 corresponds to the sum of lanthanum and scandium. EP2 corresponds only to scandium.

Table 1. Results of the potentiometric titration of rare earth elements with the Cu-ISE (n = 6).

Sample (n = 6)	Content (g/L)	Recovery (%)
Yttrium	10.07	100.9
Scandium	10.07	100.6
Lanthanum	13.88	99.6
Cerium	16.01	100.1
Neodymium	10.06	100.6

Table 2. Results of the sample mixture lanthanum and scandium by back-titration with the Cu-ISE (n = 2).

Sample (n = 2)	Content (g/L)	Recovery (%)
Lanthanum	6.88	98.7
Scandium	5.13	102.4

Table 3. Results of the REE mineral determination in «steenstrupine» by back-titration with the Cu-ISE (n = 3).

Sample (n = 3)	Content Ce(III) (g/L)	Recovery (%)
Steenstrupine	7.93	99.1

CONCLUSION

Back-titration is a cost-effective and precise alternative to conventional analytical methods, such as ICP, for determining the presence of rare earth elements. As a method of determination, potentiometric titration is flexible in handling the wide variety of REE minerals. Thanks to optimization of the analytical matrix and the use of complex chemistry, it can even separate certain REEs from each other in mixtures.

The automated system with the OMNIS Sample Robot S – WSM equipped with an OMNIS Titrator, OMNIS Dosing Modules, and copper-selective electrode, impresses with its high level of professionalism and offers flexible analyses combined with high-end software.

REFERENCES

1. Misumi, S.; Taketatsu, T. Complexometric Titration of Rare Earth Elements. Dissolution of the Rare Earth Oxalate with Ethylenediaminetetraacetic Acid and Back Titration with Magnesium Sulfate. *bull. Chem. Soc. Jpn.* **1959**, *32* (8), 873–876. DOI:10.1246/bcsj.32.873
2. Seel, F. Die Komplexometrische Titration. Die Chemische Analyse. Band 45. Von G. Schwarzenbach Und H. Flaschka. Ferdinand Enke Verlag, Stuttgart 1965. 5. Neubearbeitete Aufl., XVI, 339 S., 42 Abb., 12 Tab., 48,– DM. *Angewandte Chemie* **1966**, *78* (8), 455–455. DOI:10.1002/ange.19660780817
3. *Chelates in Analytical Chemistry – A Collection of Monographs*; Flaschka, H. A., Barnard, A. J., Eds.; Marcel Dekker, Incorporated, 1967; Vol. 3.
4. Krebs, D.; Furfaro, D. Concentrated Hydrochloric Acid Leaching of Greenland Steenstrupine to Obviate Silica Gel Formation. In *Rare Earth Elements - Emerging Advances, Technology Utilization, and Resource Procurement*; IntechOpen, 2022. DOI:10.5772/intechopen.107012

CONTACT

瑞士万通中国
北京市海淀区上地东路1号
院1号楼7层702
100085 北京
marketing@metrohm.com.cn

CONFIGURATION

OMNIS Sample Robot S – WSM (1T/2P)

OMNIS Sample Robot S – WSM 配备 1 个 OMNIS Workstation Module,包括 2 台用于清洁和抽吸传感器及样品容器的泵、1 个工作站、棒式搅拌器以及丰富的全自动滴定直接入门附件。该系统的 2 个样品架提供了容纳 32 只样品杯,每只 120 mL 的位置。这套模块化系统在完整安装状态下提供,因此可以在最短时间内启动。根据要求还可以为系统升级另外 2 台蠕动泵以及另一个工作站,以使吞吐量加倍。如果需要其它工作站,Sample Robot S 可升级为 L 尺寸的 OMNIS Sample Robot,这样可以在最多 4 个工作站上同时加工 7 个样品盘的样品,达到四倍样品吞吐量。

OMNIS Professional Titrator

创新型、模块式电位分析 OMNIS Titrator,用于进行终点和等当点滴定(单一/动态)。由于采用 3S OMNIS Liquid Adapter 技术,处理化学品从未像现在一样安全。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。包括用于使用其他滴定或加液模块平行滴定的“Professional”功能许可证。

- 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最多四个滴定模块或加液模块
- 可以扩展磁力搅拌器和/或棒式搅拌器
- 可提供不同大小的计量管:5、10、20 或 50 mL
- 采用 3S 技术的 OMNIS Liquid Adapter:安全处理化学品,自动传输生产厂家的原始试剂数据

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 5 路平行滴定:“Professional” 功能许可证

OMNIS Dosing Module

用于与 OMNIS Titrator 滴定仪相连的加液模块,以扩展额外用于滴定/加液的滴定管。可以扩展磁力搅拌器和/或螺旋搅拌器,以作为单独的滴定台使用。可自由选择 5、10、20 或 50 mL 计量管单元。

Cu

具有晶体膜的铜选择性电极。

这种 ISE 必须搭配参比电极使用,并且适用于:

- Cu2+ 的离子测量
- 小样品体积的离子测量(最小浸没深度为 1 mm)
- 用 CuEDTA 进行络合滴定

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。