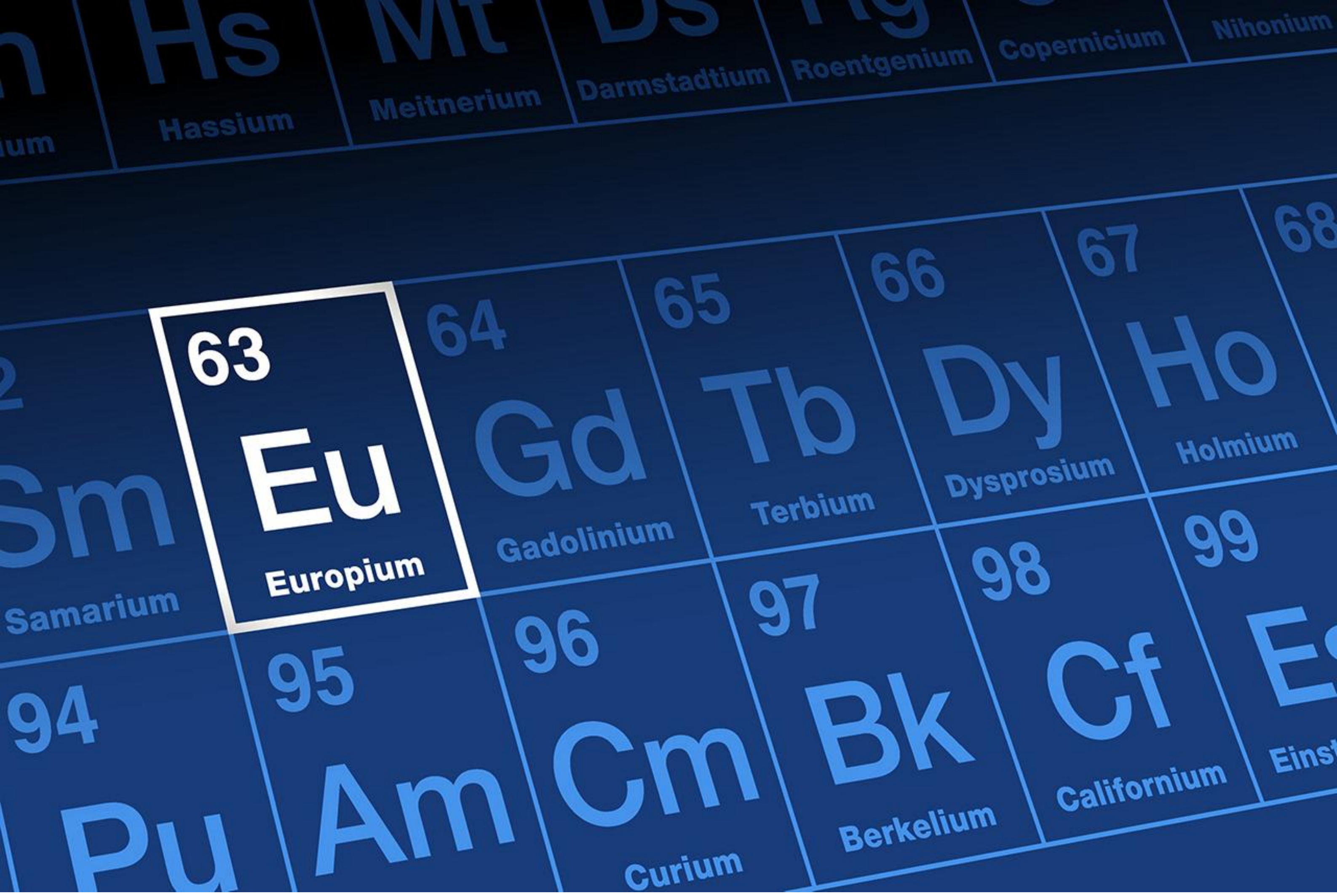

Application Note AN-T-250

Potentiometric analysis of rare earth elements (REEs)

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.

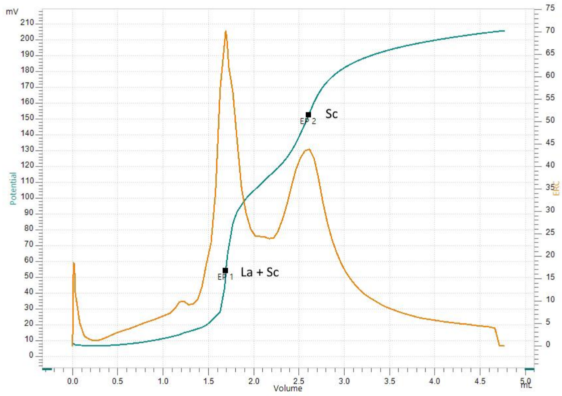

Figure 2. Back-titration of a mixture of lanthanum and scandium with the Cu-ISE. EP1 corresponds to the sum of lanthanum and scandium. EP2 corresponds only to scandium.

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.

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CONFIGURATION

OMNIS Sample Robot S – WSM (1T/2P)

OMNIS Sample Robot S – WSM, equipped with an OMNIS Workstation Module with 2 pumps for cleaning and extraction of the sensors and sample vessels, a workstation, rod stirrers, and extensive accessories for getting started directly with fully automated titration. The system provides space in two sample racks for 32 sample beakers of 120 mL each. This modular system is supplied completely installed and can thus be put into operation in a very short time. The system can also be extended upon request to include 2 additional peristaltic pumps and another workstation, thus doubling the throughput. If additional workstations are required, then the Sample Robot S can be extended to become an L-sized OMNIS Sample Robot, thus enabling samples from 7 racks to be processed in parallel on up to 4 workstations to quadruple the sample throughput.

OMNIS Professional Titrator without stirrer

Innovative, modular potentiometric OMNIS Titrator for endpoint titration and equivalence point titration (monotonic/dynamic). Thanks to 3S Liquid Adapter technology, handling chemicals is safer than ever before. The titrator can be freely configured with measuring modules and cylinder units and can have a stirrer added as needed. Including "Professional" function license for parallel titration with additional titration or dosing modules.

- Actuation via PC or local network
- Connection option for up to four additional titration or dosing modules for additional applications or auxiliary solutions
- Can be supplemented with magnetic stirrer and/or rod stirrer
- Various cylinder sizes available: 5, 10, 20 or 50 mL
- Liquid Adapter with 3S technology: Safe handling of chemicals, automatic transfer of the original reagent data from the manufacturer

Measuring modes and software options:

- Endpoint titration: "Basic" function license
- Endpoint and equivalence point titration (monotonic/dynamic): "Advanced" function license
- Endpoint and equivalence point titration (monotonic/dynamic) with 5-way parallel titration: "Professional" function license

OMNIS Dosing Module without stirrer

Dosing module for connection to an OMNIS Titrator for extending the system to include an additional buret for titration/dosing. Can be supplemented with one magnetic stirrer or rod stirrer for use as separate titration stand. Freely selectable cylinder unit with 5, 10, 20 or 50 mL.

Ion-selective electrode, Cu

Copper-selective electrode with crystal membrane.
This ISE has to be used in combination with a reference electrode and is suitable for:

- ion measurements of Cu^{2+} (10-8 to 0.1 mol/L)
- ion measurements in small sample volumes (minimum immersion depth 1 mm)
- Complexometric titrations with CuEDTA

Thanks to the robust/break-proof plastic shaft made of EP, this sensor is mechanically very resistant.
The polishing set supplied enables easy cleaning and renewing of the electrode surface.