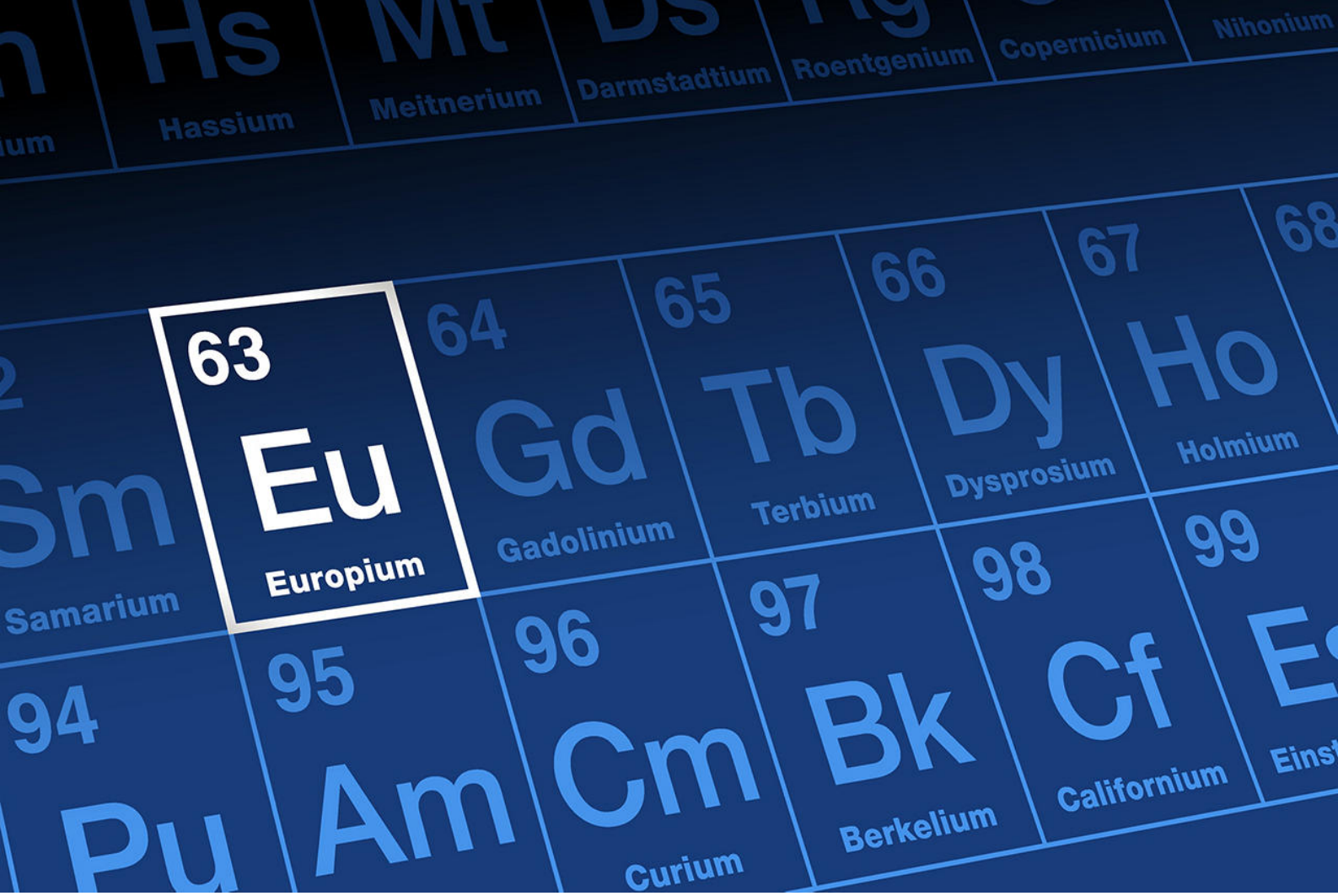

Application Note AN-T-250

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 → Ln(EDTA)

$CuSO_4$ + $EDTA_{(excess)}$ → 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.

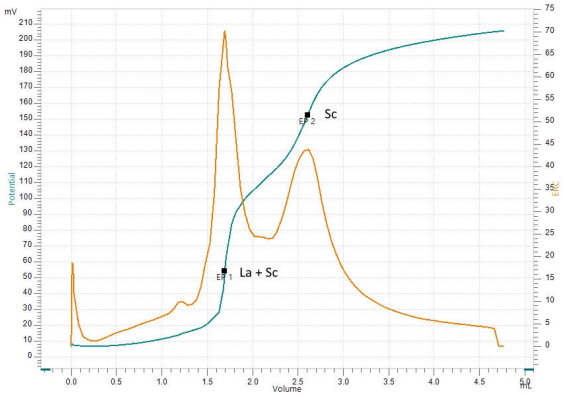

Figure 2. Back-titration of a mixture of lanthanum and scandium with the Cu-ISE. EP1 corresponds to the sum of lanthanum and scandium. EP2 corresponds only to scandium.

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 equipado con un OMNIS Workstation Module con 2 bombas para limpiar y aspirar los sensores y recipientes de muestras, 1 puesto de trabajo y agitador de varilla, así como una extensa gama de accesorios para acceder directamente a la titulación completamente automática. Este sistema ofrece en 2 gradillas de muestras espacio para 32 vasos de muestra de 120 mL cada uno. Este sistema modular se suministra totalmente montado y, por ello, puede ser puesto en funcionamiento en muy poco tiempo. Si se desea, el sistema puede ampliarse con 2 bombas peristálticas más y otro puesto de trabajo, para así duplicar el rendimiento. Si fueran necesarios más puestos de trabajo, el Sample Robot S puede ampliarse con un OMNIS Sample Robot del tamano L, de modo que se puedan procesar paralelamente muestras de 7 gradillas en hasta 4 puestos de trabajo para cuadriplicar así la capacidad en cuanto al número de muestras.

OMNIS Professional Titrator sin agitador

OMNIS Titrator, innovador, modular y potenciométrico para la titulación a punto final y la titulación a punto de equivalencia (monótona/dinámica). Gracias a Liquid Adapter con tecnología 3S, este titulador resulta más seguro que nunca para el manejo de productos químicos. El titulador se puede configurar libremente con módulos de medida y unidades de cilindro y, si es necesario, se le puede anadir un agitador. Incluye la licencia funcional "Professional" para la titulación en paralelo con módulos de titulación o dosificación adicionales.

- Control a través de ordenador o red local
- Posibilidad de conexión de hasta 4 módulos de titulación o dosificación más para otras aplicaciones o soluciones auxiliares
- Ampliable con agitador magnético y/o agitador de varilla
- Diferentes tamanos de cilindro disponibles: 5, 10, 20 o 50 mL
- OMNIS Liquid Adapter con tecnología 3S: manejo seguro de productos químicos, transferencia automática de los datos originales del reactivo del fabricante

Modos de medida y opciones de software:

- Titulación a punto final: licencia funcional "Basic"
- Titulación a punto final y titulación a punto de equivalencia (monótona/dinámica): licencia funcional "Advanced"
- Titulación a punto final y titulación a punto de equivalencia (monótona/dinámica) con titulación quíntuple en paralelo: licencia funcional "Professional"

OMNIS Dosing Module sin agitador

Módulo de dosificación para la conexión de un titulador OMNIS para incluir una bureta adicional de titulación/dosificación. Se puede ampliar con un agitador magnético o de varilla para su uso como stand de titulación independiente. Libre selección de la unidad de cilindro con 5, 10, 20 o 50 mL.

Electrodo ion-selectivo, Cu

Electrodo selectivo de cobre con membrana de cristal.

Este electrodo ion-selectivo debe utilizarse en combinación con un electrodo de referencia y es adecuado para:

- Medidas de iones de Cu2+ (10-8 hasta 0,1 mol/L)
- Medidas de iones en volúmenes de muestra muy pequenos (profundidad de inmersión mínima = 1 mm)
- Titulaciones complexométricas con CuEDTA

Gracias a un eje de plástico EP robusto y a prueba de roturas, este sensor puede soportar altas cargas mecánicas.

El kit de pulido suministrado facilita la limpieza y la regeneración de la superficie del electrodo.