Enhanced Detection of Rare Earth Elements Using Inductively Coupled Plasma Atomic Emission Spectrometry with Ultrasonic Nebulization

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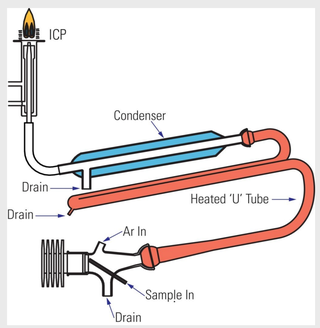
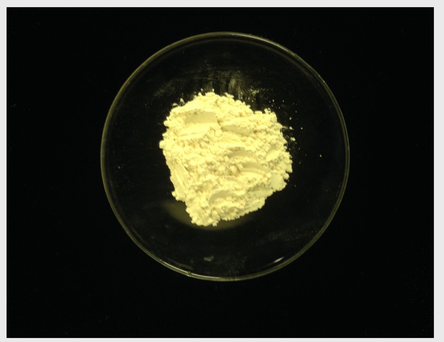
Abstract: The rare earth elements (the 15 lanthanides plus yttrium and scandium) are critical components of modern alloys, batteries, catalysts, ceramics, glasses, magnets, and phosphors. Specific applications of rare earth elements (REEs) include use in hybrid cars, wind turbines, and computer hard disk drives. Characterization of ore samples for REE levels is thus a very important analytical task, and inductively coupled plasma atomic emission spectrometry (ICP-AES) with conventional pneumatic nebulization can be used to detect trace levels (microgram/L) of REEs in solution. This poster will examine REE detection limits that can be achieved using ICP-AES with a more efficient ultrasonic nebulizer (USN). Figures of merit in a dilute nitric acid matrix will include instrument detection limits (IDLs) and LOQs (limits of quantitation). In addition, a commercial grade cerium oxide matrix will be analyzed with the ultrasonic nebulizer / ICP-AES combination to measure elemental impurities and IDLs of various rare earths.



Teledyne CETAC U5000AT+ USN & Schematic

PerkinElmer 5300DV ICP-AES & USN



Cerium (IV) Oxide Powder

Instrumentation:

1. ICP-AES: PerkinElmer Optima 5300DV ICP-AES
2. Ultrasonic Nebulizer: Teledyne CETAC U5000AT+

Reagents:

1. Nitric Acid, Optima grade, Fisher Scientific, Fairlawn, NJ, USA
2. Hydrogen Peroxide, TraceSelectGrade, >30%, Fluka Analytical, Sigma Aldrich Chemie, Steinheim, Germany
3. Various single element standards, Inorganic Ventures, Christiansburg, VA, USA

Sample:

1. Cerium (IV) Oxide, 99.9%, GFS Chemicals, Powell, OH, USA

Cerium (IV) Oxide Sample Preparation

Cerium (IV) Oxide:

2.01 g of the cerium (IV) oxide sample was added to a precleaned 500-mL PFA bottle. The following reagents were added in order to the PFA bottle: 10mL of deionized water, 10-mL of high-purity grade nitric acid, and 10-mL of high-purity grade hydrogen peroxide. [1]

The PFA bottle with sample and reagents was placed on a hot plate set to low heat for 30 minutes. The cerium (IV) oxide dissolved to provide a clear solution.

The resulting solution was diluted to 200mL with deionized water to yield a 1% (w/v) sample of cerium(IV) oxide.

1. L. Zhaofen, M. Chasseau, Horiba Scientific, ICP Application Note #61.

ICP-AES Calibration with Std. Neb. & USN

Standards:

1. One set of calibration standards containing 20, 50, 100, and 200 µg/L Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sc, Sm, Tb, Th, Tm, U, Y, Yb, was used to calibrate the ICP-AES with the standard pneumatic nebulizer and the ultrasonic nebulizer (USN). The reagent blank and all standard were prepared in 1% high-purity nitric acid using pre-cleaned 125-mL low-density polyethylene (LDPE) bottles.
2. Following calibration the reagent blank was introduced with both nebulizers to determine the instrument detection limit (IDL) and limit of quantitation (LOQ); the former is defined as 3x the standard deviation of the blank concentration, the latter as 10x the standard deviation of the blank concentration.
3. An additional calibration in a 0.1% CeO_2 matrix was performed for Ho, Lu, Sm, Tm, Yb, Ba, Ca, Fe, Mg, Si, and Zn; complex background emission was less pronounced for these elements.

ICP-AES Operating Conditions – Std. Neb.

ICP Power:	1300 W
Plasma Gas:	15 L/min
Auxiliary Gas:	0.2 L/min
Nebulizer Gas:	0.60 L/min
Resolution:	Normal
Viewing:	Simultaneous, Axial
Torch Injector:	Alumina, 2 mm diam.
Torch Position:	-2
Points/peak:	3
Integration Time:	20 sec min, 20 sec max
Replicates:	3
Pneumatic Nebulizer (PN):	Glass Concentric
Spray Chamber:	Glass Cyclonic
Sample Uptake Rate:	1.5 mL/min (pumped)

ICP-AES Operating Conditions - USN

U5000AT+ USN operating conditions are the same as the standard nebulizer except for the parameters listed below. The USN was connected to the host ICP-AES using Teledyne CETAC interface kit SP8140. Setup time is approximately 5 minutes, including removal of the standard nebulizer/spray chamber. The ICP torch and injector were not changed.

Nebulizer Gas:	0.55 L/min
Torch Position:	-4
USN Interface Kit:	SP8140, 5 min setup
Sample Uptake Rate:	2.0 mL/min (pumped)
Heater Temperature:	140°C
Condenser Temperature:	3°C

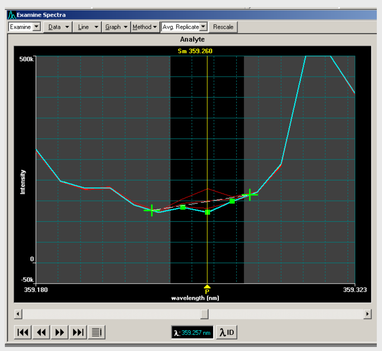
Signal Intensities in 1% HNO_3

Element (λ,nm)	Std. Neb, 100ppb	USN, 100ppb	Factor
Ce (413.764)	6016	58323	9.7
Dy (353.170)	42026	670597	15.9
Er (337.271)	39065	607012	15.5
Eu (381.967)	118301	1659431	14.0
Gd (342.247)	26711	338351	12.6
Ho (345.600)	36777	535874	14.5
La (408.672)	47305	615216	13.0
Lu (261.542)	114143	1329123	11.6
Nd (406.109)	13498	182508	13.5
Pr (414.311)	11128	147702	13.2
Sc (361.383)	240095	2924656	12.1
Sm (442.434)	21893	333936	15.2
Tb (350.917)	12138	169452	13.9
Th (283.730)	3989	42572	10.6
Tm (313.126)	41218	591126	14.3
U (424.167)	11520	179316	15.5
Y (371.029)	201385	2491265	12.3
Yb (328.937)	258423	3436205	13.2

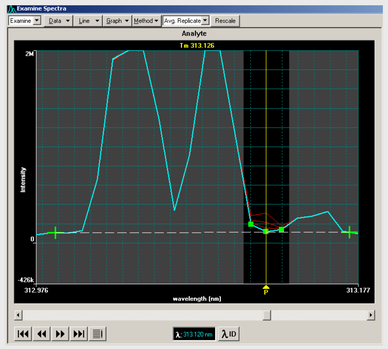
IDL and LOQ Comparison in 1% HNO_3

Element (λ, nm)	IDL (Std. Neb, USN) µg/L	LOQ (Std. Neb., USN) µg/L	IDL Factor
Ce (413.764)	2.3, 0.13	7.6, 0.43	18
Dy (353.170)	0.33, 0.01	1.1, 0.033	33
Er (337.271)	0.26, 0.01	0.86, 0.03	26
Eu (381.967)	0.05, 0.002	0.16, 0.007	25
Gd (342.247)	0.32, 0.02	1.05, 0.07	16
Ho (345.600)	0.16, 0.008	0.53, 0.026	20
La (408.672)	0.35, 0.006	1.15, 0.02	58
Lu (261.542)	0.03, 0.003	0.1, 0.01	10
Nd (406.109)	0.7, 0.02	2.3, 0.07	35
Pr (414.311)	0.96, 0.02	3.1, 0.07	48
Sc (361.383)	0.04, 0.002	0.13, 0.007	20
Sm (442.434)	1.1, 0.03	3.6, 0.1	36
Tb (350.917)	0.46, 0.03	1.5, 0.1	15
Th (283.730)	1.5, 0.04	4.9, 0.13	37
Tm (313.126)	0.35, 0.01	1.1, 0.03	35
U (424.167)	1.5, 0.04	4.9, 0.13	37
Y (371.029)	0.04, 0.002	0.13, 0.007	20
Yb (328.937)	0.02, 0.0008	0.07, 0.003	25

Sm (359.260nm) in 0.1% CeO_2, ICP-AES & USN



Tm (313.126 nm) in 0.1% CeO_2, ICP-AES & USN



IDLs in 0.1% CeO_2 with Std. Neb & USN

Element (λ, nm)	Std. Neb. IDL (µg/L)	USN IDL (µg/L)	Factor
Ho (345.600)	1.49	0.24	6.2
Lu (261.542)	0.07	0.15	0.46
Sm (359.260)	0.96	0.18	5.3
Tm (313.126)	0.87	0.94	0.92
Yb (289.138)	0.94	0.13	7.2
Ba (233.527)	0.37	0.38	0.97
Ca (317.933)	0.31	0.09	3.4
Fe (259.939)	0.25	0.53	0.47
Mg (285.213)	0.25	0.30	0.83
Si (251.611)	0.28	0.18	1.5
Zn (213.857)	0.43	0.13	3.3

➢ Complex background from CeO_2 matrix; need for higher resolution and/or additional emission lines (ex. sequential ICP-AES)