Application Note: 40770

Reduction of Refractory Oxide Polyatomic Interference Using Kinetic Energy Discrimination

Thermo Scientific XSERIES 2 ICP-MS with 3rd Generation CCTED

Key Words

- Collision Cell Technology (CCT)
- Kinetic Energy Discrimination (KED)
- Oxide Interference

Introduction

Refractory elements, such as cerium can react with oxygen-bearing species in an ICP to form metal oxide (MO^+) polyatomic species which can interfere with other analytes of interest. An example of this is the interference of isotopes of barium oxide (BaO^+) with rare earth elements such as samarium, gadolinium and europium.

Collision / reaction cells have been used to remove or reduce many polyatomic species and attempts have been made at developing methodologies for reactively removing such refractory metal oxide species. One such method used oxygen to react the MO^+ species to higher oxides such as MO_2^+, leaving the analyte free of interference.[1] Unfortunately, since the formation of oxide species can be undesirable and may cause the loss of analyte sensitivity (at best) and the formation of new interferences (at worst), this approach is not universally applicable. Similarly, the effectiveness of this approach depends upon the kinetics of the reaction gas and the interfering species.

A preferable situation would be the simultaneous removal or reduction of all polyatomic species with the use of a single cell gas. Du and Houk demonstrated the ability to reduce metal oxides under specific conditions with the use of helium cell gas.[2.] Unknowingly, this was the first reported description of kinetic energy discrimination (KED). Realizing the significance of this phenomenon, researchers at Thermo Fisher Scientific refined their 1998 collision cell and developed a new collision cell specifically designed to incorporate kinetic energy discrimination operation. This was released in 2001 in the Thermo Scientific X Series ICP-MS. It has since been comprehensively re-designed with major improvements giving our 3rd generation collision cell in the XSERIES 2 ICP-MS. This design incorporates a new cell entry lens arrangement that controls the ions entering the cell by virtue of ion energy, a new post-cell chicane lens arrangement that aids energy discrimination and analyte ion transmission under KED conditions in addition to giving the lowest continuum background of any ICP-MS, and new electronics to improve analyte transmission in KED mode.

A convenient method of assessing the effectiveness of kinetic energy discrimination for removal of metal oxide species is by measuring the signal intensity ratio of cerium oxide (CeO^+) to cerium (Ce^+). Cerium is chosen since it has a particularly high affinity for combination with oxygen and cerium oxide has a strong bond that is not easily dissociated in the plasma (CeO bond enthalpy = 795 kJ mol^{-1}).

Method

A 100 ppb solution of cerium in dilute (1%) nitric acid was used to test the ability of the XSERIES 2 3rd generation CCTED to reduce metal oxides. Scans were collected over the relevant mass regions to indicate the signal strength for cerium and cerium oxide. Peak centre measurements were also made in order to calculate CeO^+/Ce^+ ratios. Ratios are, by convention, expressed as a percentage by multiplying the ratio by 100.

Instrument Configuration

A Thermo Scientific XSERIES 2 was fitted with the Xs interface option and CP Grade helium (BOC Speciality Gas Products, Basingstoke, UK) was used as the cell reagent gas. The gas was purified with a nickel catalyst in-line gas purifier (model IG-35 XL, Johnson Matthey Pureguard). Various instrument settings were used. Critical values are shown with the results to which they pertain.

Results

In standard mode of operation (cell unpressurised), the CeO/Ce level was measured at 1.0 %. Signal intensity and oxide formation were observed to increase with modest helium gas flow rates. The highest cerium transmission was observed with a helium flow rate of around 3.5 mL/min and no kinetic energy barrier. Above this gas flow rate, sensitivity begins to reduce. When the kinetic energy barrier is increased in the positive direction, Ce sensitivity reduces with a concomitant, but more rapid, reduction in the transmission of cerium oxide.
Ce sensitivity decreases more rapidly with increasing gas flow rate as the KED volts are increased. The CeO transmission decreases more rapidly than that of Ce with increasing gas flow rate as the KED barrier is increased. This behavior is described by the surface plots given in Figure 1. The CeO/Ce ratio reflects this, with the lowest ratios produced by settings with higher gas flows and KED voltages (see Figure 2). There is a trade-off, however, between producing low oxide ratios and retaining cerium sensitivity. The amount of sensitivity traded-off for a given oxide ratio is a good indicator of the effectiveness of the kinetic energy discrimination. Table 1 gives data for the Ce sensitivity, corresponding CeO intensity and the CeO/Ce ratio (as %) under three instrument conditions. The conditions relate to positions 1., 2. and 3. in Figure 2.

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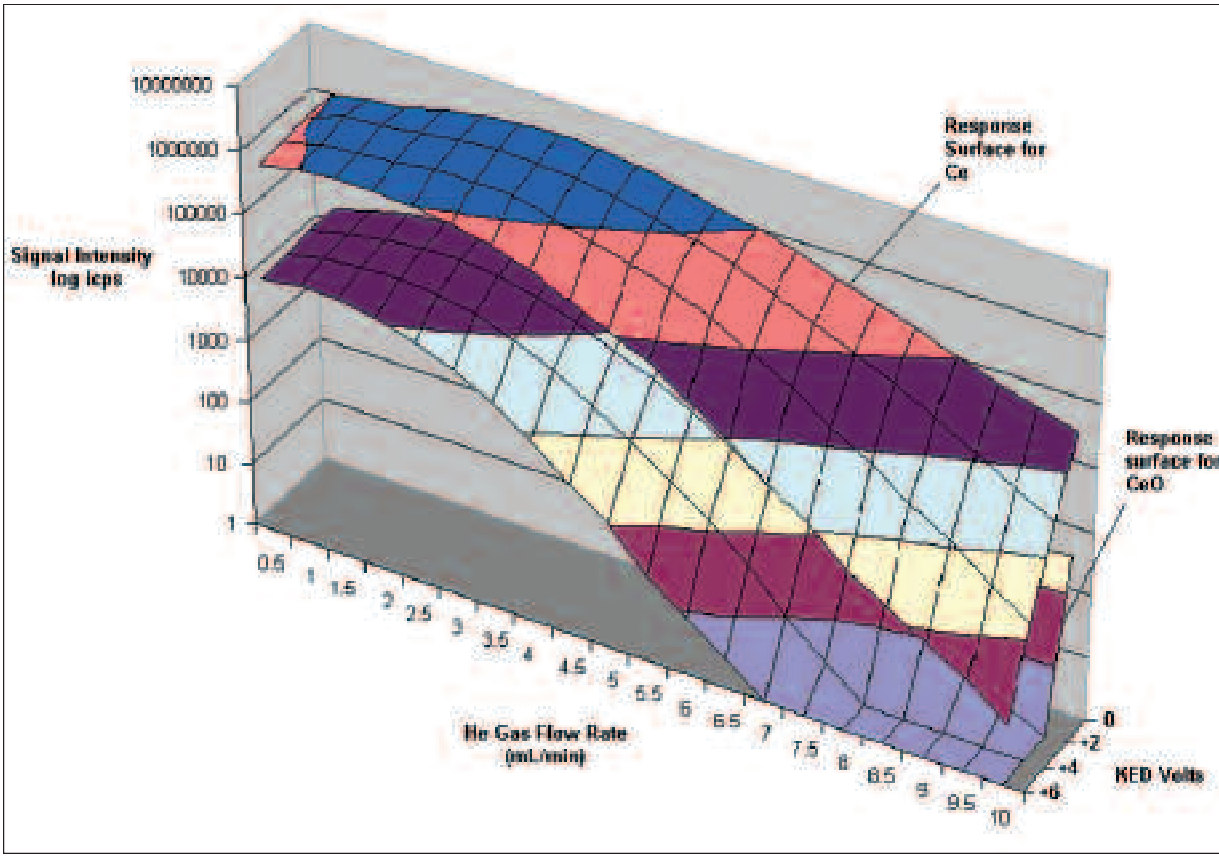


Figure 1: Response Surfaces for Ce and CeO

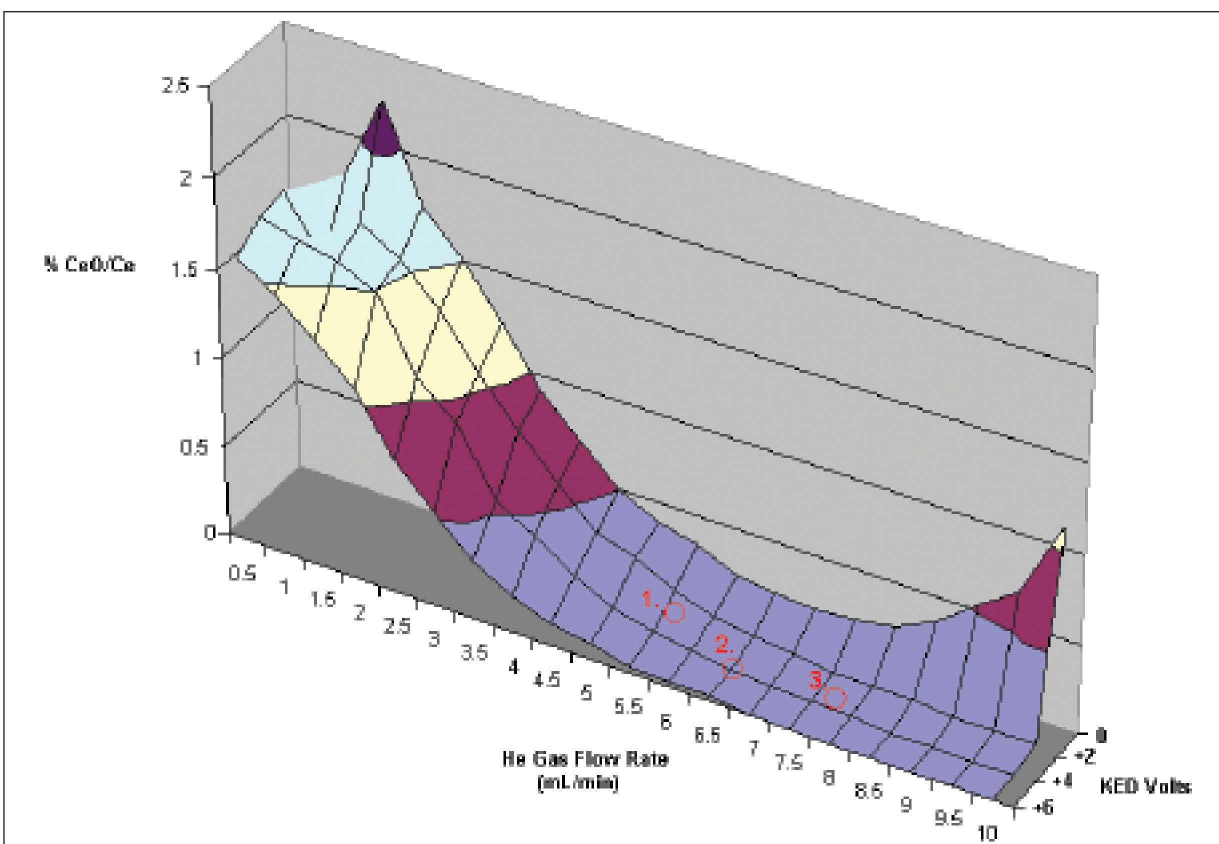


Figure 2: Response Surface for CeO/Ce (%)

Table 1 shows that under typical KED conditions (condition set 1.), good sensitivity is attained (~10 Mcps/ppm), whilst very low oxides are observed (0.15 %). Conditions 2. and 3. indicate that much lower oxide contributions can be achieved (0.06 and 0.02 %, respectively) by sacrificing a little sensitivity. The oxide ratio attained under condition set 3. (0.03 %) is the lowest cerium oxide ratio ever reported from any ICP-MS. Scans for these values are shown in Figures 3, 4, and 5.

Cond[a]	KED Volts	He FLOW (mL/min)	Ce (icps)	CeO (icps)	CeO/Ce (%)
1	3	5.5	996246	1512	0.152
2	4	6.3	192820	121	0.063
3	3.5	7.5	60069	16	0.027

Table 1: Cerium Sensitivity and Oxide for Various KED Conditions

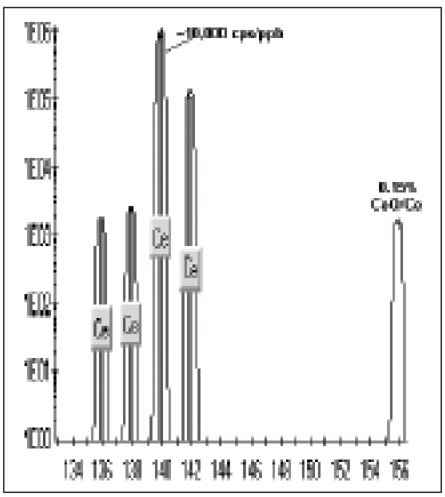


Figure 3: Scan for 100 ppb Ce (Condition 1.)

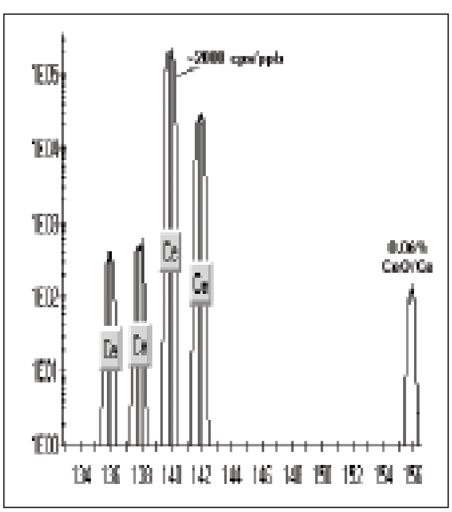


Figure 4: Scan for 100 ppb Ce (Condition 2.)

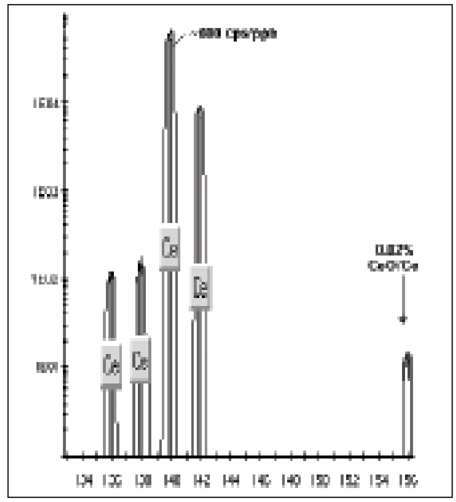


Figure 5: Scan for 100 ppb Ce (Condition 3.)

Conclusion

The Thermo Scientific XSERIES 2 ICP-MS offers the ability to reduce refractory oxide interferences to negligible levels when operated in helium KED mode. This mode has the added benefit of removing other polyatomic species under a single set of conditions. The level of CeO/Ce ratio reduction (compared to standard mode operation) combined with the level of Ce sensitivity retained is a good measure of the effectiveness of kinetic energy discrimination. Efficacious KED requires good control of ion energy distribution prior to the cell, effective reduction in the energy of unwanted species in order to separate the energy distributions as much as possible, followed by good transmission of analyte species and effective rejection of unwanted polyatomics. The performance shown in this note demonstrates the capability of our 3rd generation CCT^ED to reduce CeO to an unprecedented level, whilst retaining Ce transmission. This indicates the unequalled effectiveness of our kinetic energy discrimination approach due to our unique pre-cell π-lens and post-cell chicane lens.

References

1. L.A. Simpson, M. Thompsen, B.J. Alloway, A. Parker, *J. Anal. At. Spectrom.*, 2001, **16**, 1375-1380

2. Z. Du and R.S. Houk, *J. Anal, At. Spectrom.*, 2000, **15**, 383-388.

Plasma Capabilities from Thermo Fisher Scientific

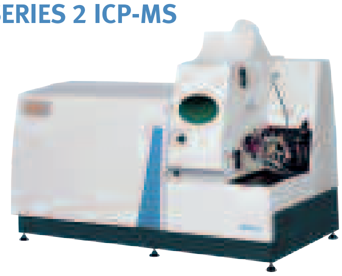
The use of an Inductively Coupled Plasma source (ICP) is the accepted and most powerful technique for the analysis and quantification of trace elements in both solid and liquid samples. Its applications range from routine environmental analyses to the materials industry, geological applications to clinical research and from the food industry to the semiconductor industry.

Thermo Fisher Scientific is the only instrument manufacturer to offer the full range of Inductively Coupled Plasma Spectrometers (ICP, Quadrupole and Sector ICP-MS) to satisfy every aspect of plasma spectrometry from routine to highly demanding research applications.

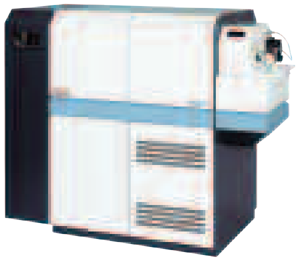
Develop your lab from the easy-to-use iCAP ICP to the high performance XSERIES 2 Quadrupole ICP-MS and up to the ultra-sophisticated ELEMENT2 and NEPTUNE Sector ICP-MS instruments. Each instrument combines leading-edge technology, fit for purpose and affordability with a tradition of quality, longevity, accuracy and ease of use.

Thermo Scientific iCAP ICP

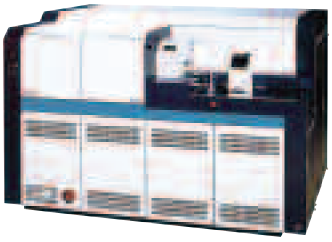
Thermo Scientific XSERIES 2 ICP-MS



Thermo Scientific ELEMENT2 HR-ICP-MS



Thermo Scientific NEPTUNE Multi-collector ICP-MS



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