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OXIDES BY HPLC/IDMS

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ABSTRACT Since the early seventies IDMS (isotopic dilution mass spectrometry) has been used at the Institutt for energiteknikk for the determination and certification of rare earth elements in high purity Y_2O_3 . These lanthanides have, during the last few decades, become more widely used in high technology. High purity, quality 4 N (99.99 %) or even 5 N materials are needed for phosphors, lasers, optical fibers, x-ray films, and recently as an important constituent in contrast fluids for MRI (magnetic resonance imaging). However in a matrix consisting primarily of a single lanthanide, IDMS alone will not be effective due to isobaric interferences from the main elements or the mono-oxides formed in the ion source. On the other hand HPLC (high performance liquid chromatography) can be used, but the detection limit will be in the order of 5-10 ppm/W. In this work a combination of HPLC/IDMS has been used to lower the detection limit to 1 ppm/W, where the sample is spiked before separation by HPLC, followed by IDMS analysis of the HPLC-fractions. In some cases the HPLC-process had to be repeated to remove the main element completely. Results are presented for Dy_2O_3 and Nd_2O_3 , but for the other rare earth oxides similar separating procedures can be applied.			
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1. HISTORICAL

Since the early seventies IDMS (isotopic dilution mass spectrometry) has been used at the Institutt for Energiteknikk for the determination of rare earth elements in high purity Y_2O_3 . (1).

For easy work, a mixture is made of all spikes which can be used: "The master spike".

The formed mono-oxides from the light elements will interfere with the natural ions of the heavier elements but in an yttrium matrix this can be avoided by introducing benzene into the ion-source at a constant flow rate of 0.5 torr through a gold-leak as reported in 1969. (2). The mono-oxides will disappear and representative peaks are obtained.

The lanthanides have during the last few decades become more widely applied in high technology. High purity (quality) 4 N (99.99%) or even 5 N materials are needed for phosphors, lasers, optical fibers, x-ray films and recently as an important constituent in contrast fluids for MRI (magnetic resonance imaging). However in a matrix consisting primarily of a single lanthanide, IDMS alone will not be effective due to isobaric interference from the main element or the mono-oxides from this element formed in the ion-source.

On the other hand HPLC can be used, but the detection limit will be 5 ppm/W. In this work a combination of HPLC and IDMS was used to lower the detection limit to 1 ppm/W, which will be sufficient for most requirements.

Case-studies were carried out on 2 commercial products Dy_2O_3 and Nd_2O_3 and results are presented here. For other rare earth oxides similar separating processes can be set up.

2. EXPERIMENTAL

2.1 THE HPLC SEPERATION METHOD

A modification of the method of R.M. Cassidy (3) was used for the determination of REE in Dy_2O_3 and Nd_2O_3 by HPLC. The detection limit was 5 ppm/W. The following equipment was used:

Spectra-Physics IsoChrom pump
Spectra-Physics Spectra 100 detector set at 512 nm
Supelcosil 5 micron C18 25 cm x 4.6 mm column
Valco model c6u injector
LDC model 308 integrator

The samples were dissolved in concentrated nitric acid, evaporated to dryness and dissolved in a mixture of 0.1 N hydroxyisobutyric acid (HIBA) and 0.5 N n-octanesulfonic acid (OS). Sample solutions corresponding to up to 1 mg of the oxide were injected on the column. An eluent of 0.10 N HIBA and 0.01 N OS was used for the determination of Tb in Dy_2O_3 . For the determination of the other REE a stepwise gradient from 0.15 N, 0.30 N and 0.60 N HIBA and 0.01 N OS was adopted. For the determination of REE in Nd_2O_3 all REE were eluted with 0.2 N HIBA except La which was eluted with 0.6 N HIBA. Pr could not be determined directly in the Nd-solution because the Nd-peak overlapped the Pr-peak.

2.2 THE IDMS METHOD

A varian TH5 mass spectrometer with a therm-ion source and a single secondary electron multiplier collector was used. A known amount of the sample was mixed with a known amount of the master spike, dissolved and about 1 μ l of the solution was loaded on the Re-filament. The filament material was zone-refined Re-ribbon obtained from Cross Company, Mass. USA, and was preheated before use. After loading the prepared cartridge into the mass spectrometer the heating current and registration programme had to be kept strictly.

The "master spike" was a solution of the different spikes in a known concentration in diluted nitric acid. The following spikes were used: Ce₁₄₂, Nd₁₄₅, Sm₁₄₉, Eu₁₅₁, Gd₁₆₀, Dy₁₆₁, Er₁₇₀ and Yb₁₇₃. All obtained from ORNL (Oak Ridge National Laboratory). La (always contaminated with Ba₁₃₈), Lu (contaminated with Yb₁₇₆) and the mono-isotope elements Pr, Tb, Ho and Tm, were compared with other multiple elements acting in almost the same way and registered at the same time in the current and registration programme.

Only small corrections had to be applied after experimental research with known amounts of the two elements involved. In this way La is compared with Ce, Pr with Eu, Tb with Gd and Ho, Tm, Lu with Er.

3. THE HPLC/IDMS METHOD

3.1 Nd₂O₃

In a mass spectrum of Nd all masses from 142 to 150 will be contaminated with high Nd peaks. Similar will all masses from 158 to 176 have NdO peaks. On the other hand the determination by HPLC will give results in the range from 5-10 ppm (table 1, column 1).

A combination of the two methods where HPLC was used to remove all of the Nd from an in advance spiked sample gave results down to the 1 ppm level. Prior to the injection of the sample on the HPLC-column an exact amount of spike solution was added to the dissolved sample and mixed well.

The HPLC-fractions were combined and evaporated to dryness. The Pr-fraction was injected one more time on the column in order to remove all the Nd. To remove the OS the residue was treated for 24 hours in a Low Temperature Ashing Unit, dissolved in a few microliters of hydrochloric acid and loaded on the Re-filament for MS-analysis. Approximately 5 µg of high purity yttrium was also applied to the filament. This was found to have a stabilizing effect on the ion beam. The results are given in table 1, column 2.

Table 1. Nd_2O_3

Element	ppm by HPLC	ppm by HPLC/IDMS
La	< 10	\leq 3
Ce	< 10	< 3
Pr	—	50
Sm	< 5	1.8
Eu	6	2
Gd	< 10	< 1
Tb	< 5	< 1
Dy	< 10	< 1
Ho	< 5	< 1
Er	< 5	< 1
Tm	< 5	< 1
Yb	< 5	< 1
Lu	< 5	< 1

3.2 Dy_2O_3

In a matrix of Dy direct IDMS determination of Gd, Tb, Ho, Yb, Tm and Lu is not possible due to isobaric interference from Dy-isotopes, tailing effects from Dy-isotopes and the influence of mono-oxides. La, Ce, Pr, Nd, Sm and Eu on the other hand can be analysed directly.

HPLC was used to remove the Dy from the spiked sample. The fractions were collected, evaporated to dryness, treated in Low Temperature Ashing Unit and measured by mass spectrometry. Again 5 μg of high purity Y was applied to the filament to get a more stable ion beam. Due to the Dy_2O_3 -fabrication process the sample contained larger amounts of Gd, Tb and Ho and these could directly be analysed by HPLC. The results were verified by HPLC/IDMS. Chromatograms from this analysis are shown in fig. 1 and 2. The results for the Dy_2O_3 -sample are shown in table 2.

Table 2. Dy₂O₃

Element	ppm by HPLC/IDMS	ppm by HPLC
La	< 1	< 5
Ce	0.5	< 5
Pr	< 1	< 5
Nd	< 0.5	< 5
Sm	1	< 5
Eu	1.2	< 5
Gd		70
Tb		220
Ho		10
Er	< 0.5	< 5
Tm	< 1	< 5
Yb	< 0.5	< 5
Lu	< 1	< 5

SUMMARY

Both HPLC and IDMS can be used to analyse rare earth elements in a rare earth-oxide matrix. However both methods have their limitations due to interference-problems, isobaric effects or detection limits.

A combination of both methods has shown to be a powerful tool to cope with this problems. The results have shown a sufficient low detection limit, as defined by the present market for use of rare earth in high technology, can be achieved. For other rare earth oxides similar procedures can easily be adopted.

In press:

More detailed description off the HPLC/IDMS method with improved detection limits and results from Gd²⁰³ are to be published in an article with the following title:

"Determination of rare earth elements in high purity rare-earth oxides by liquid chromatography and combined liquid chromatography isotope dilution mass spectrometry"

by H. Stray, D.E. Stijfhoorn and H. Hjelmseth
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Work Report CH-97 (1972), Institutt for Atomenergi now Institutt for Energiteknikk, Kjeller, Norway.
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J. Haaland and D.E. Stijfhoorn,
Procedings XV Colloguim Spectroscopicum International, III,
1969 Madrid.
3. R.M. Cassidy, Chemical Geology, 67 (1988) 185-195.

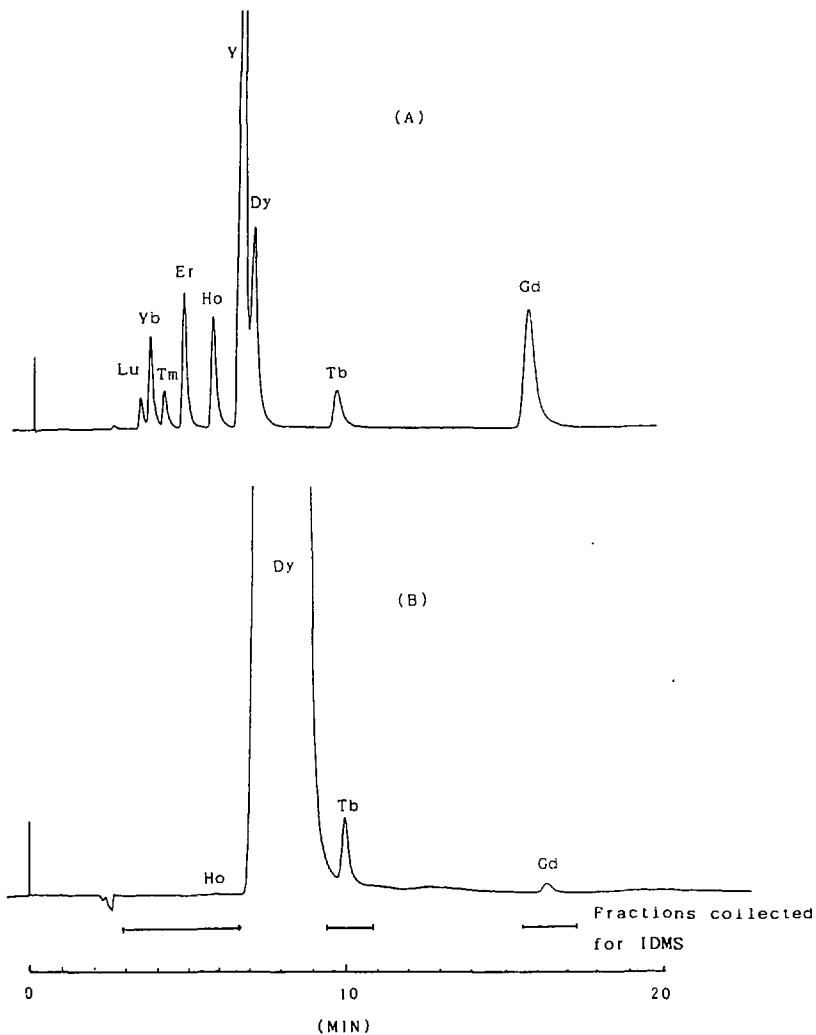


Fig.1 HPLC chromatograms of (A): Standard solution containing 43.3 ng Lu, 120 ng Yb, 40 ng Tm, 121 ng Er, 79 ng Ho, 400 ng Y, 125 ng Dy, 37 ng Tb, 168 ng Gd, and (B): solution of 0.18 mg Dy_2O_3 . Eluent 0.10 N HIBA 0.01 N OS

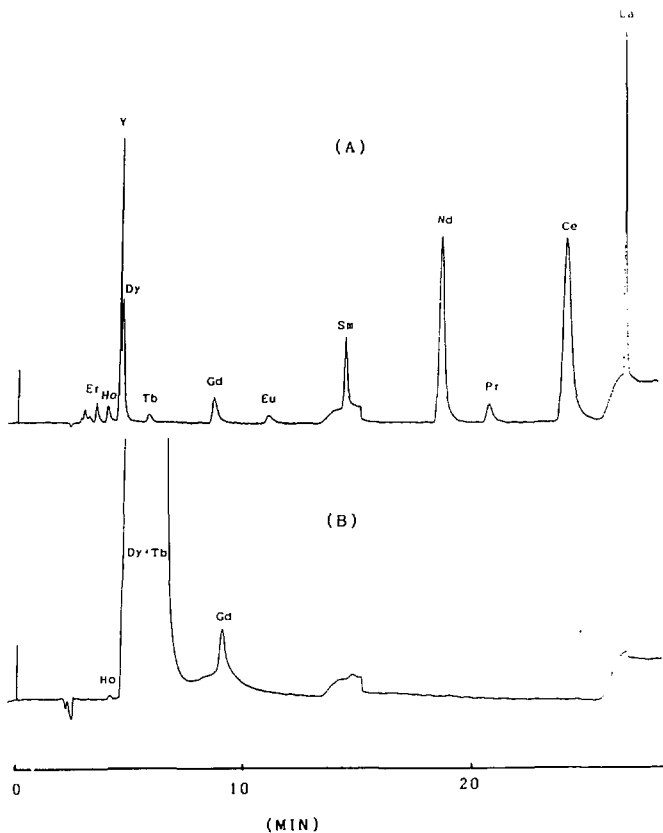


Fig.2 HPLC chromatograms of (A): 15 ng Er, 9 ng Ho, 50 ng Y, 15 ng Dy, 5 ng Tb, 21 ng Gd, 30 ng Sm, 123 ng Nd, 17 ng Pr, 168 ng Ce, 98 Ng La, and (B): solution of 0.36 mg of Dy_2O_3 . Stepwise gradient from 0.15 N HIBA to 0.30 N HIBA after 10 min., and to 0.60 N HIBA after 22 min.

Institutt for energiteknikk (IFE) (tidligere Institutt for atomenergi) ble grunnlagt i 1948 og etablert som en uavhengig stiftelse i 1953. Hovedsenteret ligger på Kjeller. Virksomheten i Halden er konsentrert om det internasjonale OECD Halden Reactor Project.

IFE er, med sine 540 ansatte, et av de største teknologiske forskningsinstitutter i Norge.

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Institutt for energiteknikk (IFE) (formerly Institutt for atomenergi) was founded in 1948, and established as an independent foundation in 1953. The main center is located at Kjeller. The activities in Halden are concentrated on the international Halden OECD Reactor Project. IFE, with its 540 employees, is one of the major technological research institutes in Norway.

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