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# Determination of Rare Earth Elements in Several Alloys by Graphite Furnace Absorption Spectrometry with Ascorbic Acid as Modifier

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## Summary

Using of concentrated HCl as a solvent and ascorbic acid ($C_6H_8O_6$) as a chemical modifier is advantageous to the determination of La, Sm, Pr, Nd in several alloys by graphite furnace atomic absorption spectrometry. Adding ascorbic acid of 1.0g/L as a chemical modifier to the samples, there results in pyrolysis temperature of 1 000, 1 000, 1 200°C and 1 200°C for La, Sm, Pr and Nd, and atomization temperature of 2 700°C for all samples, respectively. With the use of integral absorption, a limit of detection of 341μg/L, 16μg/L, 874μg/L and 572μg/L are found for La, Sm, Pr and Nd, respectively.

*Keywords*: rare earth elements; sensitivity; GFAAS; Modifier; alloy

## 1. Introduction

Recently, rare earth elements (REEs) are widely used in special material science, and therefore manufacturing and application of REEs are being rapidly developed. REEs are used in steel, iron and ferro–magnet materials as well as electronic materials, fluorescence materials, catalysts, optical glass and glass grinders. The physical and chemical properties of these special materials are considerably influenced by the amounts of REEs additives and impurities. Common additives are La, Sm, Pr and Nd of REEs, and it is important to determine amounts of them in materials, since the mechanical and electronic properties of materials are directly changeable by them [1, 2, 11, 13].

Some researchers studied about the dissipation processes and the formation of condensed phase species in GFAAS by using digital imaging techniques [4]. The difficulties of determination of REE traces have been extensively studied [6].

L'vov and co–workers used tantalum lined graphite tubes for REE determinations with various spectroscopic techniques. This condition made an increase in sensitivity compared to PG tubes; in addition, the memory effects were diminished. They also combined the Ta–lined furnace with a Ta platform to conduct an experiment for determination of the REEs [7, 8].

Other researchers found that the use of a tungsten platform is advantageous to the determination of REEs, since direct contact of the carbide–forming sample with carbon is avoided and in the formation of tungsten carbide it prevents the REEs from carbide formation [6]. They also proved that application of the highest possible atomization temperature can apply, especially, in the presence of REE matrices. another people used the tungsten atomizers [10] for REE determinations, for providing with a faster heating rate, vaporization and atomization processes become faster compared to graphite furnaces.

In the present work, the GFAAS technique was applied to study the atomization process of La, Sm, Pr and Nd in the samples. The possibility of pre–concentration of REEs by the selective evaporation of the matrix was investigated, and then the proper atomization and pyrolysis temperatures were found.

## 2. Experiments

### 2.1 Instrumentation and conditions

GFAAS experiments were carried out by Z–5000 (Hitachi High Technology, Japan) with pyrolysis graphite tube (Model 190–6003) and an auto–sampler. La, Sm, Pr and Nd signals were measured at 550.1nm, 484.2nm, 513.3nm and 463.4nm, respectively. Hollow cathode lamps were respectively operated at 14.5, 15.0, 15.0 and 15.0mA current and Zeeman background correction was used for background correction with a spectral slit of 0.2nm.

High purity argon (99.9%) was employed as a purge gas. The measurements were taken after injecting 20μL volume of solutions onto the pyrolysis graphite tube. The integrated absorbance $A_{int}$ signals were measured for 5.0s. The GFAAS operating conditions are summarized in Table 1.

**Table 1.** GFAAS operating conditions

| Step | Temperature, °C | | Time, s | | Ar gas flow rate, L/min |
|---|---|---|---|---|---|
| | start | end | ramp | hold | |
| Drying | 140 | 200 | 40 | 0 | 200 |
| Pyrolysis | 1 000[a] | 1 000 | 20 | 0 | 200 |
| Atomization | 2 700[b] | 2 700 | 0 | 5 | 30 |
| Cleaning | 2 800 | 2 800 | 0 | 4 | 200 |
| Cold | 0 | 0 | 0 | 17 | 200 |

a. Varied in optimization studies between 800°C and 2 200°C at atomization temperature of 2 700°C.

b. Varied in optimization studies between 1 800°C and 2 800°C at pyrolysis temperature of 1 000°C.

## 2.2 Reagents

The chemicals used in the experiment were of analytical grade (Merck). Deionized and doubly distilled water was used to dilute the solutions. Stock solutions of La, Sm, Pr and Nd (1g/L) were prepared from high purity oxides in the same manner as the samples. Stock solutions were prepared as high purity oxides were dissolved by HCl, after diluting with 5.0mol/L HCl. A stock solution of ascorbic acid chemical modifier 1.0 g/mL was prepared from high purity ascorbic acid (Merck) dissolved in doubly distilled water.

## 2.3 Preparation of samples

It was found that dissolution of mixture of REEs was rapid in HCl, compared to oxide acids [3]. Therefore, the powdered samples were dissolved in concentrated HCl and diluted to obtain 1.0mol/L HCl concentrations. For determination of REEs in several alloys, the sample solutions were prepared as following; the species of 0.1~0.2g with accuracy of 0.000 1g. After that it were dissolved in HCl (20%, v/v), and diluted to 100~250mL after adding chemical modifier of proper concentration.

## 3. Results and discussion

### 3.1 Pyrolysis and atomization steps

The characteristic mass $m_0$ is proportional to the energy of oxide dissolution, and atomization of species is considerably relative to oxide dissolution. [5, 12] The pyrolysis and atomization curves of La, Sm, Pr and Nd are shown in Fig. 1, which were measured with the integrated absorbance $A_{int}$ signals.
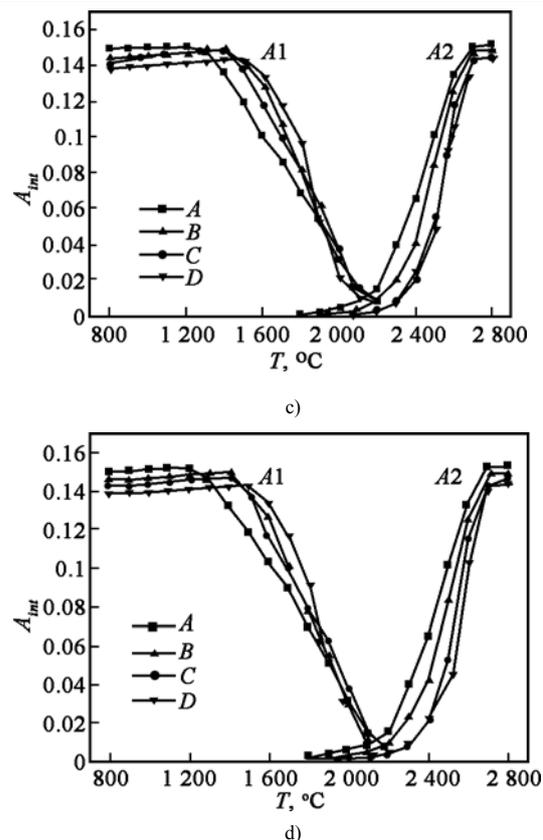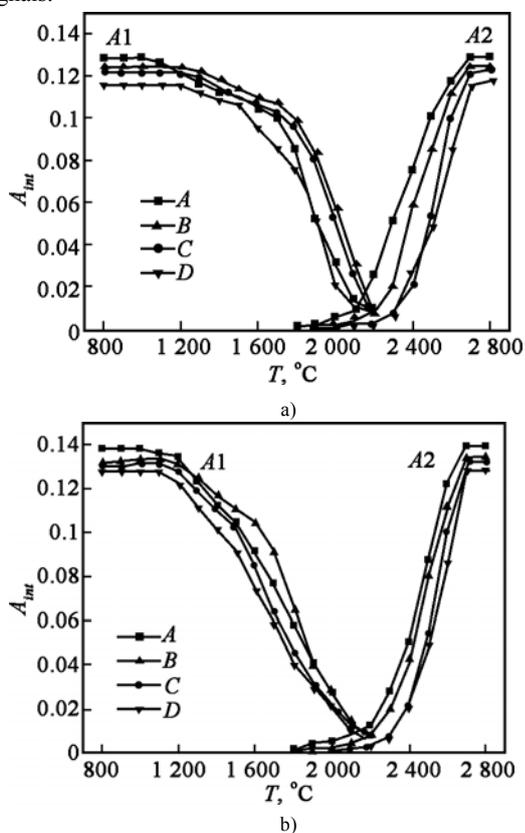
a)

b)

c)

d)

**Figure 1.** Thermal pyrolysis 1 and atomization 2 curves for La, Sm, Pr, Nd; (a) HCl+matrix+modifier; (b) HCl+matrix; (c) HNO₃+matrix+modifier; (d) HNO₃+matrix; concentrations: RE; 1.0mol/L HCl; 100g/L Fe, Al; 1g/L ascorbic acid.

According to curves $A$1 from Fig.s 1, the optimal maximum pyrolysis temperature is approximately 1 200, 1 100, 1 400 and 1 400°C for La, Sm, Pr and Nd in HCl medium respectively. Applying matrix in HCl medium, optimal maximum pyrolysis temperatures remain practically unchanged (curves 1). When adding ascorbic acid chemical modifier to the matrix and HCl medium, the curves 1 shows optimal maximum pyrolysis temperature of 1 000°C for La and Sm, and 1 200°C for Pr and Nd. As shown in the atomization curves of A2 in Fig. 1, the appearance temperature $T_{app}$ is between 2 100°C and 2 300°C for La, Sm, Pr and Nd. When adding chemical modifier to the HCl medium, the atomization curves of La and Sm are lower than without chemical modifier. For Pr and Nd, it does not change. In nitric acid medium without the matrix, the optimal maximum pyrolysis temperatures were 1 200°C, 1 100°C, 1 400°C and 1 400°C for La, Sm, Pr and Nd, respectively, and they increased to approximately 1 500°C for Pr and Nd, with the matrix. The $T_{app}$ values in former case were 2 100°C, 2 100°C, 2 200°C and 2 200°C, and the $T_{app}$ values in latter case were 2 300°C. The $T_{app}$ in matrix free conditions were related to the dissociation of REEs monoxides in the gas phase. The optimal maximum pyrolysis temperature and $T_{app}$ values of La, Sm, Pr and Nd in nitric acid and hydrochloric acid medium are close. Therefore, it explains that the vaporization takes place from the same chemical form in both medium, which should be the oxide form. Consequently, the chloride salts is hydrolyzed

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almost completely in the drying and pyrolysis steps. In this carbide formation, it is essential that the pyrolysis step lasts a relatively long time so that this solid state reaction can proceed. Since atomization of the carbide is less than of the oxide, the absorption signal in the pretreatment step is decreased.

### 3.2 Interference effects of matrix

For determination of La, Sm, Pr and Nd by using atomic absorption spectrometry, it is mandatory to completely remove matrix interference. In order to remove matrix interference, separating matrix or adding chemical modifier procedures can be used. The procedures of separating matrix are complex, so that loss of analyzes or contamination by impurities can be bringing. However, through using the chemical modifiers, the accurate determination results would be obtained without separating procedures. Considering prior literatures, in this study some organic chemical modifiers are chosen, such as triammonium citrate, ascorbic acid and tartaric acid. The test results show in Table 2.

**Table 2.** The effects of various chemical modifiers(recovery, %).

| chemical modifier | $C$, g/L | Interference elements, $10^3$ folds | | | |
|---|---|---|---|---|---|
| | | La | Pr | Nd | Sm |
| triammonium citrate | 0.0 | 89.7 | 89.3 | 88.2 | 89.4 |
| | 0.5 | 93.2 | 93.5 | 93.8 | 93.4 |
| | 1.0 | 94.8 | 94.7 | 94.0 | 94.8 |
| | 1.5 | 95.1 | 94.6 | 95.7 | 95.9 |
| | 2.0 | 95.6 | 94.2 | 94.4 | 94.9 |
| ascorbic acid | 0.0 | 92.1 | 92.9 | 93.0 | 92.5 |
| | 0.5 | 94.3 | 94.5 | 94.9 | 94.3 |
| | 1.0 | 97.5 | 97.9 | 98.0 | 97.9 |
| | 1.5 | 96.8 | 96.7 | 96.0 | 96.4 |
| | 2.0 | 95.1 | 95.0 | 95.7 | 95.9 |
| tartaric acid | 0.0 | 87.3 | 88.0 | 87.9 | 88.7 |
| | 0.5 | 90.2 | 90.8 | 91.2 | 91.6 |
| | 1.0 | 92.2 | 93.0 | 93.6 | 93.9 |
| | 1.5 | 92.3 | 92.5 | 92.1 | 92.1 |
| | 2.0 | 91.8 | 91.4 | 91.9 | 92.4 |

As seen in Table 2, the recovery rate significantly increases when using chemical modifiers. Ascorbic acid among them has good effects. Because the major fraction of chloride matrix is released from the furnace in the previous heating step and mono−chlorides are formed in the atomization step, the effects of a chemical modifier are not good for Pr and Nd. The retardation of a small fraction of volatile matrices in the cooler ends of the graphite tube is a known phenomenon [4], and the vaporized fraction of the previously condensed chloride matrix and its diffusion to the central part of the tube can result in mono−chloride formation in the gas phase.

At the pyrolysis step, ascorbic acid as a chemical modifier is dissolved into CO and $H_2$, which are reduction gases. These gases accelerate the atomizing from oxide phase. Therefore, at the atomization step, analytical species can be completely reduced and atomized. The proper concentration of the chemical modifier in solution was chosen as 1.0g/L.

### 3.3 Performance data of samples

The results of the determination for La, Sm, Pr and Nd in the

ferroalloy and aluminum matrix, according to the procedure described above, are depicted in Table 3.

**Table 3.** The determination results for La, Sm, Pr and Nd in practical samples ($n$=5).

| sample | Results, $10^{-3}$% | | | |
|---|---|---|---|---|
| | La | Pr | Nd | Sm |
| sample 1(matrix as Fe) | 5.4±0.2 | 4.1±0.1 | 1.8±0.1 | 3.9±0.3 |
| sample 2(matrix as Fe) | 21.0±0.6 | 7.0±0.2 | 9.0±0.5 | 41.0±2.6 |
| sample3(matrix as Fe) | 35.0±1.0 | 15.0±0.4 | 18.0±0.9 | 132.0±8.3 |
| sample 4(matrix as Al) | 11.0±0.3 | 2.0±0.1 | 2.0±0.1 | 14.0±0.9 |
| sample 5(matrix as Al) | 52.0±1.5 | 12.0±0.3 | 7.0±0.4 | 36.0±2.3 |

sample 1 consists of Fe 70.7%, Cr 18.5%, Ni 8.8%

sample 2 consists of Fe 69.9%, Cr 18.9%, Ni 9.2%

sample 3 consists of Fe 68.5%, Cr 18.8%, Ni 10.7%.

sample 4 consists of Al 92.7%, Cu 3.8%, Mg 1.5%, Mn 0.5%, and sample 5 consists of Al 91.4%, Cu 4.5%, Mg 1.8%, Mn 0.8%.

When measuring with the integral absence $A_{int}$, the limits of detection are 341μg/L, 16μg/L, 874μg/L and 572μg/L for La, Sm, Pr and Nd, respectively. The calibration curves constructed with $A_{int}$ signals are practically identical with the chemical modifier.

## 5. Conclusions

When the determination of REEs with the GFAAS, HCl medium provides better absorption signal shape, and keeps longer graphite tube life. Ascorbic acid as chemical modifier increases in the atomization effects, because it offers strong reduction environments at atomization step. This method can be effectively used to determinate REEs in several alloys and several environment samples.

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