

The determination of La, Ce, Pr, Nd, Ni, Co and Mn in rare earth hydrogen storage alloy (AB₅ Type) by inductively coupled plasma atomic emission spectrographic method

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La, Ce, Pr, Nd, Ni, Co and Mn, in a rare earth hydrogen storage alloy (AB₅ type) are determined by inductively coupled plasma atomic emission spectrographic method. The analytical lines are selected by studying the spectrum overlap interference of single elemental matrix. The matrix concentration being kept at 0.2 mg/ml, a matrix depression effect can be ignored. The recovery ratios and relative standard deviations of this analytical method range from 82% to 129% and from 2.2% to 11.1% respectively. A comparison of results between Inductively coupled plasma atomic emission spectrographic method and other methods is satisfactory. This analytical method has such merits as high sensitivity, rapidity, accuracy and multi-element simultaneous determination.

Key words: rare earth hydrogen storage alloy, AB₅ type, Inductively coupled plasma atomic emission spectrographic method, determination, spectrum interference.

Introduction

At present, the rare earth hydrogen storage alloy (HSA) (AB₅ type), which is initially a LaNi₅ binary alloy, is widely applied in nickel metal hydride batteries. To improve the performance and lower the production cost, MmNi₅ type (Mm: mixed rare earth metals) and MNi₅ type (Ml: La-rich mixed RE metals) compounds are used in almost all industrial production instead of the binary alloy. Some additive elements, like Mn and Co, can improve the performance of the alloy.

In the field of hydrogen storage alloy analysis, titration, gravitation and X-ray fluorescence spectrometric method, which are relatively complicated and require long process, are used traditionally. Now, a newly developing analytical method, inductively coupled plasma atomic emission spectrographic method is being used in this field due to its rapidity, multi-element simultaneous determinations. Li xinhai [1] chose the best analytical lines and corrected some interference between elements with interference coefficients in the analysis of HSA. In some corresponding literature [2], impurity elements in nickel powder were determined.

Based on these studies, a further study is made in this article on the determination of La, Ce, Pr, Nd, Ni, Co and Mn in HAS (AB₅ type).

Experimental

Chemicals

The concentrations of single element standard solutions (La, Ce, Pr, Nd, Ni, Co, Mn) are 100 µg/ml or 50 µg/ml. Deionized water and purified HCl were employed in the experiments.

Apparatus

Perkin-Elmer 2000 type inductively coupled plasma atomic emission spectrometer

Analysis Procedures

100 mg HSA sample was weighed into a 100 ml beaker and slowly dissolved by addition of 10 ml HCl (1+1) until the solution is clear. The sample solution was made up in a matrix concentration of 0.2 mg/ml whose acidity was 1% (HCl).

The multi-element standard series solutions, whose acidity was the same as that of the sample solution, were made up by mixing and diluting the single element standard solutions. They were to be determined by inductively coupled plasma atomic emission spectrometer with the sample solution. The concentrations of the standard series solutions are given in Table 1.

Table 1. Standard series solutions concentration (µg/ml)

Elements	S ₀	S ₁	S ₂	S ₃	S ₄	S ₅	S ₆
La, Ce, Pr, Nd, Co, Mn	0.0	1.0	2.0	5.0	10.0	20.0	50.0
Ni	0.0	20.0	50.0	100.0	140.0	200.0	—

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Results and Discussion

Selection of Analytical Lines

As each element has many atomic emission spectrum lines, it is very common that spectral lines of different elements overlap with each other. So, for Inductively coupled plasma atomic emission spectrographic method, the selection of the analytical lines is important and necessary.

The selection principle is that the selected line of the element to be determined should have high sensitivity and be less overlapped by the lines of other coexisting elements.

To study the interference resulted from the main coexisting elements (La, Ce, Pr, Nd, Ni, Mn, Co) of HSA, the single element standard solutions (La 100 $\mu\text{g/ml}$, Ce 100 $\mu\text{g/ml}$, Pr 100 $\mu\text{g/ml}$, Nd 100 $\mu\text{g/ml}$, Ni 100 $\mu\text{g/ml}$, Co 50 $\mu\text{g/ml}$, Mn 50 $\mu\text{g/ml}$) were determined at those selected analytical lines.

From Table 2, the overlapping interferences resulted from the coexisting elements are too low to be considered. In a practical determination of HSA, the concentration ranges of the main coexisting elements are 20–30 $\mu\text{g/ml}$ (La), 30–40 $\mu\text{g/ml}$ (Ce), 2–4 $\mu\text{g/ml}$ (Pr), 10–20 $\mu\text{g/ml}$ (Nd), 40–60 $\mu\text{g/ml}$ (Ni), 10–20 $\mu\text{g/ml}$

(Co), 10–20 $\mu\text{g/ml}$ (Mn), that is to say, all of them are below 100 $\mu\text{g/ml}$. Thus the interferences resulted from the main coexisting elements can be ignored. To compare the results of different lines and avoid any error resulted from spectrum line deviation, two analytical lines are used for each element.

Study of the matrix effect

A matrix depression effect, which results in negative errors, is inherent in the inductively coupled plasma atomic emission spectrographic method. An internal standard method is a good way to correct the matrix depression effect. However, the matrix depression effect will be low enough to be ignored when the matrix concentration is below some level. Under these conditions, as a simpler method, a standard curve method can replace the internal standard method.

To study whether the matrix depression effect could be ignored when the matrix concentration was kept at 0.2 mg/ml, the sample solution was determined with both a standard curve method and an internal standard method. 5.0 $\mu\text{g/ml}$ Sr was used as the internal standard in the internal standard method. Table 3 provides the comparison results.

In Table 3, the results of the two methods are almost same. So the depression effect of 0.2 mg/ml matrix to the elements determined can be ignored. In this article, the standard curve method was employed, whose operating procedure is simpler than that of the internal standard method.

Precision

According to the contents of elements in HSA, two standards with different concentrations were added into the determined solution for each element, and then determined for recovery ratios. The relative standard deviations (A sample was determined for 11 times) were calculated for each element. They were given in Table 4.

In Table 4, the recovery ratios range from 82.0 to 129.0%. The relative standard deviations range from 2.2 to 11.1%. These data represent good precision and repeatability.

Table 2. Spectrum interferences resulted from the main coexisting elements ($\mu\text{g/ml}$)

analytical lines (nm)	matrix						
	Ni	Mn	Co	La	Ce	Pr	Nd
La 333.749	-0.3	-0.2	-0.2	—	-0.1	-0.2	-0.1
398.852	-0.2	-0.1	-0.1	—	-0.2	-0.1	-0.2
Ce 413.380	0.1	0.3	0.3	0.1	—	0.0	-0.8
413.765	-0.2	-0.3	-0.4	-0.3	—	-1.4	0.4
Pr 417.942	0.1	0.1	0.0	0.3	0.5	—	2.8
422.535	0.0	0.2	0.0	0.0	-0.1	—	-1.2
Nd 406.109	0.2	0.3	0.0	0.2	-0.3	1.2	—
430.357	0.1	0.0	0.1	-0.2	0.2	4.0	—
Co 236.379	-0.2	-0.4	—	-0.3	-0.3	-0.4	-0.3
238.892	0.1	0.0	—	0.0	-0.3	0.0	0.0
Mn 259.373	-0.1	—	-0.1	-0.1	-0.1	-0.1	-0.1
257.610	-0.2	—	-0.2	-0.3	-0.3	-0.3	-0.3

Table 3. Comparison between the standard curve method and the internal standard method

Analytical lines (nm)	Standard curve method ($\mu\text{g/ml}$)	Internal standard method ($\mu\text{g/ml}$)	Analytical lines (nm)	Standard curve method ($\mu\text{g/ml}$)	Internal standard method ($\mu\text{g/ml}$)
La 333.749	28.0	28.7	Co 236.379	20.5	19.8
398.852	27.5	28.2	238.892	21.1	20.8
Ce 413.380	41.2	42.4	Mn 259.373	10.0	9.8
413.765	38.9	40.0	257.610	10.7	10.4
Pr 417.942	3.3	3.1	Ni 232.003	92.2	96.8
422.535	3.5	3.3			
Nd 406.109	13.3	13.4			
430.357	13.3	13.5			

Table 4. Recovery ratio and Relative Standard Deviation

Element	Analytical lines (nm)	Recovery ratio (%)		Average (μg/ml)	Standard Deviation (μg/ml)	Relative Standard Deviation (%)
		10.0 μg/ml added	20.0 μg/ml added			
La	333.749	96.0	94.0	27.7	0.6	2.2
	398.852	111.0	99.0	27.4	0.9	3.3
Ce	413.380	98.0	99.0	41.7	1.1	2.6
	413.765	117.0	99.0	38.6	1.8	4.7
Pr	417.942	99.0	100.0	2.7	0.3	11.1
	422.535	90.0	90.0	3.5	0.3	8.6
Nd	406.109	103.0	93.5	13.1	0.5	3.8
	430.357	94.0	95.0	12.8	0.3	2.3
Ni	232.003	108.0	100.3	93.5	2.6	2.8
Co	236.379	127.5	129.0	19.7	1.4	7.1
	238.892	102.5	94.0	19.5	1.4	7.2
Mn	259.373	82.0	106.0	10.2	0.5	4.9
	257.610	98.0	99.0	10.4	0.4	3.8

Table 5. Comparison of results between different methods (%)

Elements	Methods		
	Inductively coupled plasma atomic emission spectrographic method	X-ray fluorescence spectrometric method	Titration
La	10.52	10.83	—
Ce	17.75	17.23	—
Pr	1.42	1.60	—
Nd	5.49	5.19	—
Ni	45.68	—	45.83

Comparison of results between Different Methods

A comparison of results of the elements were made between inductively coupled plasma atomic emission spectrographic method and other methods and given in Table 5.

Considering the deviation between different analytical methods, the comparison of results of La, Ce, Pr, Nd and Ni are ideal. This proves that Inductively coupled plasma atomic emission spectrographic method can replace the traditional complicated analytical methods in the field of elemental analysis of HAS.

Conclusions

(1) In the determination of HSA elements by Inductively coupled plasma atomic emission spectrographic

method, two analytical lines are used for each element for reference. The overlap interferences resulted from the main coexisting elements to the determined elements can be ignored at these selected analytical lines.

(2) The matrix depression effect to the elements determined also can be ignored when the matrix concentration is 0.2 mg/ml. So the standard working curve method is used in the determination.

(3) The recovery ratios of all elements range from 82.0 to 129.0%, the RSDs range from 2.2 to 11.1% and the comparisons of results between Inductively coupled plasma atomic emission spectrographic method, X-ray fluorescence spectrometric method and titration are ideal.

(4) Compared with traditional analytical methods, Inductively coupled plasma atomic emission spectrographic method has such merits as high sensitivity, rapidity, accuracy and multi-element simultaneous determination. It can usefully be applied in the analysis of La, Ce, Pr, Nd, Ni, Co and Mn in HSA.

References

1. Li Xinhua, Chinese Journal of Spectroscopy Laboratory 18[2] (2001) 231-236.
2. Liu Qingping and Tian Ronghua, Environment and Development 13[4] (1998) 48-52.