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Application of low temperature electrothermal vaporization ICP-AES for determination of refractory yttrium with 1-(2-pyridylazo)-2-naphthol as chemical modifier

Shizhong Chen*, Dengbo Lu

Key Laboratory, Wuhan Polytechnic University, Wuhan 430023, PR China

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Abstract

A low temperature electrothermal vaporization inductively coupled plasma atomic emission spectrometry (ETV-ICP-AES) method was developed for the determination of the refractory yttrium, using 1-(2-pyridylazo)-2-naphthol (PAN) as chemical modifier. The trace yttrium was vaporized as PAN complex into plasma from a graphite furnace at a comparatively low temperature of 1200 °C. The operation conditions were optimized, and the vaporization behavior of Y–PAN chelate and the main factors affecting the determination were investigated in detail. Under the optimized conditions, the detection limit of Y was 0.7 ng ml^{-1}, and the relative standard deviation (R.S.D.) for 0.1 μg ml^{-1} Y was 4.5% ($n = 9$, $v = 10$ μl). The linear range of calibration curve covered three orders of magnitude. The recommended approach has been applied for analysis of three biological samples with satisfactory results. The accuracy of the method was demonstrated by analyzing two standard reference materials.

Keywords: Low temperature electrothermal vaporization; Inductively coupled plasma atomic emission spectrometry; 1-(2-Pyridylazo)-2-naphthol; Yttrium

1. Introduction

Since the first paper [1] describing the use of a tantalum filament device as a vaporizer for inductively coupled plasma atomic emission spectrometry (ICP-AES) was published in 1974, electrothermal vaporization (ETV) has developed into an important sample introduction tool for ICP-AES/MS owing to the following merits: less sample consumption, high introducing efficiency, direct solid analysis and low absolute detection limit [2–5]. However, the very low sensitivities and severe memory effects would be encountered when the conventional ETV method was applied to determining refractory elements. It is because they are difficulty to vaporize, and their more refractory carbides are often formed during the drying and vaporization stage. Fortunately, a lot of investigations indicated that the utilization of chemical modifiers, especially halogenating reagent [6–12], is a very effective approach to solve the above problems.

In recent years, the utilization of organic reagents as chemical modifiers has drawn growing attention in atomic spectrometry. Kumamaru et al. reported low temperature volatilization of the refractory elements B, Nb, V, Cr and Zr as 8-hydroxyquinolinate complexes for sample introduction in ETV-ICP-AES [13]. Tao et al. described an in situ alkylation system for the introduction of Be as diethylberylium into plasma, using ethylmagnesium bromide as a alkylation reagent [14]. The proposed method was successfully applied to determine the trace Be in aluminum-based alloys and rocks [15]. With acetylacetone and polytetrafluoroethylene (PTFE) modifiers, Wu et al. sequentially determined Cr(III) and Cr(VI) by ETV-ICP-AES [16]. In the work of Ho et al., ascorbic acid was utilized as chemical modifier for ETV-ICP-MS determination of Cr, Zn, Cd and Pb in milk powder [17]. Okamoto proposed a procedure for the determination of fluoride ion in aqueous solution by using tetraethylammonium hydroxide (TMAH) as chemical modifier at a ashing temperature of 400 °C without the loss of fluorine [18]. Ethylene diamine tetraacetic acid (EDTA) was utilized as chemical modifier for the determination of Cd, Pb and

* Fax: +86-27-83956442.
E-mail address: chenshizhong62@163.com (S. Chen).

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Hg in several fish samples by slurry sampling ETV-ICP-MS without chemical pretreatment [19]. In the previous communication [20], the trace rare earth impurities in high purity ZrO_2 were determined by low temperature ETV-ICP-AES, using 1-phenyl-3-methyl-4-benzoylpyrazolone [5] (PMBP) as a chemical modifier as well as an extractant. It is evident that organic reagent as chemical modifier may present the following advantages: (a) the vaporization temperature is much lower than that in conventional ETV and halogenating method, which is good to prolong the lifetime of vaporizer; (2) the use of the toxic and corrosive reagents such as Cl_2 and HF could be avoided in routine analysis; (3) the analytical performances could be obviously improved by combining this technique with a chemical separation/pre-concentration. Thus, the extensive research and exploitation of new organic reagent as chemical modifier may be a promising work.

As is well known, a pyridylazo reagent, 1-(2-pyridylazo)-2-naphthol (PAN) as an excellent chelating reagent, was widely used for the separation, pre-concentration and photometric analysis in analytical chemistry. Based on the relatively good thermal stability and volatility of metal–PAN complexes, some of them were previously employed for the vapor-phase sample introduction in flame atomic absorption spectrometry (FAAS) [21]. However, the application of PAN in ETV-ICP-AES has received little attention so far. The aim of this work was to explore the feasibility of PAN as chemical modifier for the low temperature electrohermal vaporization ICP-AES determination of refractory Y. The formation conditions and vaporization behaviors of Y–PAN chelate were investigated in detail. It was observed that in the present of PAN, Y could be vaporized into ICP at a comparatively low temperature of 1200 °C. The proposed method was applied to the determination of the trace Y in biological samples and standard reference materials with satisfactory results.

2. Experimental

2.1. Apparatus

An ICP spectrometric system (Beijing Second Broadcast Equipment Factory, China) with a 2 kW plasma generator was used with a conventional silica plasma torch. A WF-1B type heating device with a matching graphite furnace (Beijing Second Optics, Beijing, China) was applied for analyte vaporization. The radiation from the plasma was focused as 1:1 straight image on the entrance slit of a WDG-500-1A type monochromator (Beijing Second Optics, Beijing, China) having a reciprocal linear dispersion of 1.6 nm mm^{-1}. The evolved components were swept into the plasma excitation source through a 0.5 m long teflon tube (4 mm i.d.) by a stream of carrier gas. The transient signals were detected with a R456 type photo-multiplier tube (Hamamatsu, Japan) and a home-build direct current amplifier, and recorded by U-135 recorder (Shimadzu, Japan).

Table 1
ETV-ICP-AES operation conditions

Wavelength (nm)	371.030
Incident power (kW)	1.2
Carrier gas (Ar) flow rate (l min^{-1})	0.5
Coolant gas(Ar) flow rate (l min^{-1})	18
Observation height (mm)	12
Entrance slit width (μm)	25
Exit slit width (μm)	25
Drying temperature (°C)	100, ramp, 10 s, hold, 15 s
Ashing temperature (°C)	250, ramp, 10 s, hold, 15 s
Vaporization temperature (°C)	1200
Vaporization time (s)	4
Clear-out temperature (°C)	2600, 3 s
Sample volume (μl)	10

The instrumentation operation conditions are given in Table 1.

2.2. Standard solution and reagents

A stock standard solution of Y with 1 mg ml^{-1} was prepared by dissolving 0.2540 g Y_2O_3 (Specpure, Shanghai, China) in diluting HNO_3, and finally diluting to a volume of 100 ml with twice-distilled water. A 0.08 mol l^{-1} PAN solution was prepared by dissolving 0.1994 g PAN (Shanghai Reagent Factory, China) in 100 ml tetrahydrofuran (THF) (Shanghai Reagent Factory, China). All other reagents were of specpure grade or analytical grade. Twice-distilled water was used throughout.

2.3. Procedure

A 0.8 μg ml^{-1} Y solution was mixed with an equal volume of 0.08 mol l^{-1} PAN solution before sample introduction. After stabilizing the plasma, a 10 μl of the resulting solution was pipetted into the graphite furnace with a microsyringe. The sample inlet hole was sealed with a graphite rode before the graphite furnace heating cycle was started. According to the operating conditions given in Table 1, the analyte was vaporized and carried into the plasma by an argon carrier gas after being dried and ashied. The transient emission signal from the plasma was recorded, and the peak height was measured for quantification.

3. Results and discussion

3.1. Comparison of the signal profiles of Y with and without PAN

As a classically refractory element, Y is difficult to vaporize and determine directly by conventional ETV-ICP-AES even at a high temperature because the boiling points of both Y and its oxide are about 3500 and 4300 °C, respectively, which are much higher than 2800 °C provided commonly by conventional ETV. However, the vaporization character of Y

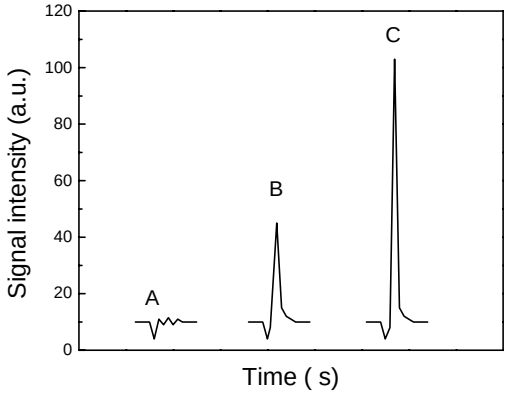

Fig. 1. Emission signal profiles for 4 ng Y vaporized at 1200 °C. (A) Y standard solution only; (B) with PAN in ethanol medium; (C) with PAN in THF medium.

changed thoroughly when PAN was added. Fig. 1 shows the typical signal profiles of Y with and without PAN as chemical modifier, and the effects of chelating reaction medium (ethanol and THF) on the signal intensity. From Fig. 1, the following conclusions can be drawn: firstly, the sharp, intense and symmetrical signal profiles of Y were recorded at a comparatively low temperature of 1200 °C after addition of PAN (B and C) duo to the formation of the volatile Y–PAN complex; secondly, no any emission signal of Y was observed at the same temperature in the absence of PAN (A); and thirdly, the signal intensity of Y in the methanol medium containing PAN (B) is about 40% of that in THF medium (C). The mechanism for the enhancement of the Y signal intensity is not fully understood right now, but it is considered to have some relation with that THF may accelerate the formation of Y–PAN chelate and stabilize it. The further examination should be carried out to explore the real reason for this.

In addition, it should be pointed out here that the emission signals of the relative blank solutions were not detected in this experiment.

3.2. Effect of ashing temperature and time on the signal intensity

Fig. 2 shows the dependence of the signal intensity of Y on the ashing temperature in the presence of PAN. It can be seen that the signal intensity of Y decreased obviously when the ashing temperature was higher than 300 °C, and the higher the ashing temperature was, the more the analyte lost due to the thermal decomposition of Y–PAN complex, which indicates that the thermal stability of Y–PAN complex was relative.

The effect of the ashing time on the signal intensity of Y was also investigated at a ashing temperature of 250 °C with PAN. The experimental result demonstrates that no significant influence was observed within the tested range of 5–30 s. Therefore, the optimum ashing temperature and ashing time in this work were 250 °C and 15 s, respectively.

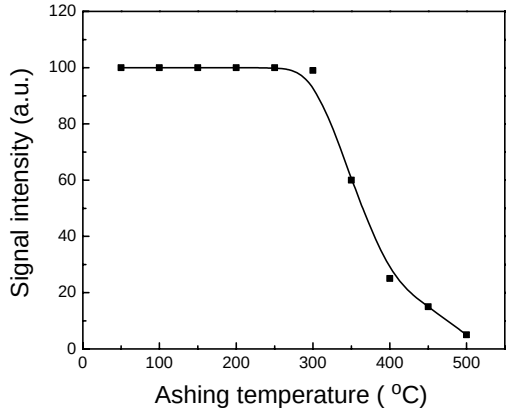

Fig. 2. Effect of the ashing temperature on the signal intensity of 4 ng Y with PAN.

3.3. Effect of vaporization temperature on the signal intensity

With and without PAN as chemical modifier, the effect of the vaporization temperature on the signal intensity of Y is shown in Fig. 3. It is clear that the addition of PAN greatly affected the vaporization behavior of Y, and its signal intensity reaches a plateau at a lower vaporization temperature of 1200 °C. This illustrates the chelating reaction between Y and PAN was complete. On the other hand, no plateau is found in the range of the tested vaporization temperature in the absence of PAN. Moreover, the Y signal intensity is much more intense with PAN than without, in despite of the application of a much higher vaporization temperature in the latter case. Thus, a vaporization temperature of 1200 °C was chosen for the determination in the following work.

3.4. Effect of vaporization time on the signal intensity

The relationship between the signal intensity and the vaporization time in the presence of PAN is given in Fig. 4. As can be seen, the maximum signal intensity of Y was

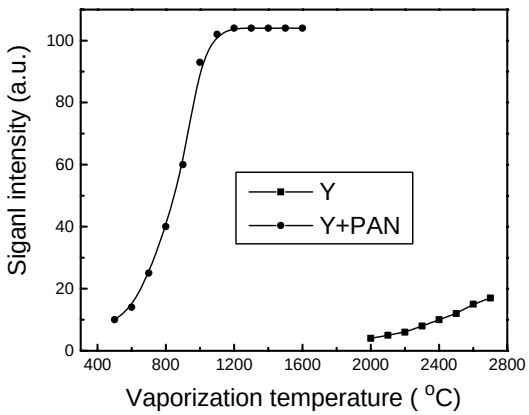

Fig. 3. Influence of vaporization temperature on the signal intensity of 4 ng Y with and without PAN.

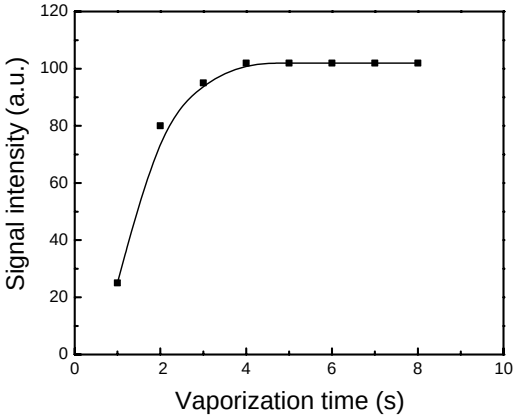

Fig. 4. Dependence of the signal intensity of 4 ng Y on vaporization time with PAN.

obtained when the vaporization time was set at greater than 3 s. This means that the vaporization of the analyte could be completes within a short time of 3 s. In the present work, a vaporization time of 4 s was utilized.

3.5. Effect of PAN concentration on the signal intensity

The effect of PAN concentration on the signal intensity of Y was studied. The results shown in Fig. 5 indicate that the signal intensities of Y depended seriously on PAN concentration. The signal intensities of Y increased remarkably with increasing PAN concentration, and the maximum signal intensity was obtained when the PAN concentration was more than 0.03 mol l^{-1}. This concentration is much more than that of Y in graphite furnace. The reasonable mechanism for the experimental fact may be that, on one hand, a large amount of extra PAN favors the formation of Y–PAN complex, while on the other hand, the vapor produced from the extra PAN in the rapid vaporization process suppresses the thermal decomposition of Y–PAN chelates. Thus, in this work the concentration of 0.04 mol l^{-1} PAN was used.

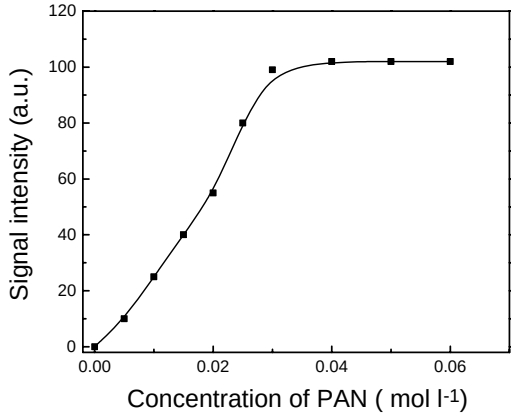

Fig. 5. Signal intensity of 4 ng Y vs. PAN concentration.

Table 2
Tolerance limits of the coexisting ions for the determination of 2 ng Y

Ion	Maximum amounts tested (μg)	Ion	Maximum amounts tested (μg)
Na^{+}	20	Cu^{2+}	0.5
K^{+}	20	Zn^{2+}	1
Ca^{2+}	10	Cr^{3+}	0.5
Mg^{2+}	10	Pb^{2+}	0.5
Ba^{2+}	10	Al^{3+}	1
Li^{+}	5	Fe^{3+}	1.5
Co^{2+}	0.4	Ni^{2+}	0.4

3.6. Effect of the foreign ions on the signal intensity

The effect of some common ions (as chlorides) on the signal intensity of Y was investigated with the addition of PAN (seen in Table 2). The tolerance amounts of coexist ions, which give an error less than 10% for the determination of analyte, were evaluated. For 2 ng Y, no significant interferences were observed from the selected metal ions at the maximum amounts tested.

3.7. Verification of the formation of Y–PAN chelate

With the addition of PAN, as described above, the vaporization character of Y was greatly improved. However, did the system really work as expected? In other word, was the Y–PAN chelate formed in ETV, vaporized and transported into ICP? To answer these questions, the following experiments were carried out. A 100 μg ml^{-1} Y solution was added into an equal volume of 0.08 mol l^{-1} PAN-THF solution. At the optimum experimental conditions, ETV was run as usual ten times with 50 μl of the resulting solution as sample. The produced sample vapor was collected in THF for the determination by ultraviolet-visible spectrophotometry (UV-Vis). The obtained absorption spectrum of the collected solution was very similar with that of Yb-PAN chelates in THF. The above experimental results indicated that PAN could indeed react with Y to form the volatile chelate.

3.8. Calibration, precision and detection limit

The analytical performance of the proposed method was determined under the optimum experimental conditions. The linear dynamic range of the calibration curve covered three orders of magnitude. The relative standard deviation (R.S.D.) of this method, obtained for nine replicate determinations at 0.1 μg ml^{-1} Y, was 4.5%. The detection limit of Y, defined as the three times the standard deviation of background noise signal intensity, was determined to be 0.7 ng ml^{-1} with PAN as chemical modifier.

3.9. Sample analysis

The proposed method was applied to the determination of the trace Y in biological samples (human hair, peach leaves

Table 3
Analytical results of Y in biological samples ($n = 5$)

Sample	ETV-ICP-AES		PN-ICP-AES
	Calibration curve method ($\mu g\,g^{-1}$)	Standard addition method ($\mu g\,g^{-1}$)	Calibration curve method ($\mu g\,g^{-1}$)
Hair	0.11 ± 0.02	0.13 ± 0.03	0.12 ± 0.01
Peach leaves	0.74 ± 0.09	0.81 ± 0.10	0.79 ± 0.05
Loulu	1.25 ± 0.13	1.13 ± 0.15	1.20 ± 0.08

Table 4
Analytical results of Y in the standard reference materials of human hair and tea leaves

Sample	Measured value[a] ($\mu g\,g^{-1}$)	Reference value ($\mu g\,g^{-1}$)
Human hair	0.093 ± 0.021	0.084 ± 0.016
Tea leaves	0.43 ± 0.05	0.36 ± 0.03

[a] Mean ± average deviation, five results.

and Chinese medicine Loulu) and standard reference materials of human hair (GBW07605) and tea leaves (GBW07601). 0.5000 g samples, dried in an air-oven at 80 °C for 5 h, were weighted accurately, and transferred into 25 ml cleaned beakers, respectively. After the samples were soaked in 10 ml concentrated nitric acid for 12 h, 2 ml perchloric acid was then added, and the samples were digested at a low temperature. The resulting solutions were vaporized to near dryness. The residues were dissolved with dilute HNO_3 and diluted to appropriate volume with doubly distilled and deionized water.

The standard solution and the sample solution were determined by standard addition method and working curve method according to the previously described procedure (Section 2.3). The results are listed in Table 3. The results mentioned above were also compared with the results obtained by pneumatic nebulization (PN)-ICP-AES. As can be seen, they are in good accordance. In addition, the standard reference material of human hair (GBW07605) and tea leave (GBW07601) were also analyzed, and the determined values are in good agreement with the certified values (see Table 4).

4. Conclusion

In summary, the use of PAN as chemical modifier in ETV-ICP-AES for the determination of the refractory Y not only effectively prohibits the formation of refractory carbides and eliminates the memory effect, but also greatly promotes the vaporization efficiency and improve the analytical sensitivity due to the formation of the good thermal stable and volatile Y–PAN complex. Further investigations can focus on the following aspects: (1) the pre-concentration procedure prior to introduction into ETV followed by the detection with ICP-AES or ICP-MS; (2) the speciation analysis of elements; (3) the direct analysis of solid sample with slurry sampling; (4) the multi-element analysis of real sample, especially rare earth elements.

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