UV-VISIBLE SPECTROPHOTOMETRY WITH ARSENAZO III FOR THE DETERMINATION OF SAMARIUM[**]

Xing-Min Guo[*], Qi-Cao Yan, Xiao-Ting Meng, Rui-Xin Ma[*]

School of Metallurgical and Ecological Engineering,
University of Science and Technology Beijing,
Beijing 100083, China; e-mail: guoxm@ustb.edu.cn; maruixin@ustb.edu.cn

UV-visible spectrophotometry with Arsenazo III is used to determine the samarium concentration. The results confirm that the concentration of Sm^{3+} in the aqueous solution from 2.7×10^{-6} to 10.8×10^{-6} mol/L obeys the Lambert–Beer law. The quantitative relationship between the absorbance and concentrations of Ca^{2+} and F^- in the solution with 2.7×10^{-6} mol/L Sm^{3+} has been obtained. The absorbance of the solution with 10.8×10^{-6} mol/L Sm^{3+} is found to be 0.58, which is not affected by the concentrations of Ca^{2+} and F^-. So, if the concentration of Ca^{2+} and F^- were known, the quantitative relationship between absorbance and Sm^{3+} concentration can be obtained, which is convenient for determining the Sm^{3+} concentration in aqueous solution with Ca^{2+} and F^- by UV-visible spectrophotometry.

***Keywords:** samarium, determination, UV-visible spectrophotometry, Arsenazo III.*

СПЕКТРОФОТОМЕТРИЯ РАСТВОРА АРСЕНАЗО III В УФ-ВИДИМОМ ДИАПАЗОНЕ ДЛЯ ОПРЕДЕЛЕНИЯ КОНЦЕНТРАЦИИ САМАРИЯ

X.-M. Guo[*], Q.-C. Yan, X.-T. Meng, R.-X. Ma[*]

УДК 543.42.062

Школа металлургического и экологического машиностроения,
Пекинский научно-технический университет,
Пекин 100083, Китай; e-mail: guoxm@ustb.edu.cn; maruixin@ustb.edu.cn

Для определения концентрации самария используется оптическая спектрофотометрия раствора Sm с Арсеназо III. Показано, что концентрация Sm^{3+} в водном растворе в диапазоне 2.7×10^{-6}–10.8×10^{-6} моль/л подчиняется закону Ламберта–Бера. Получена количественная взаимосвязь между оптической плотностью и концентрацией Ca^{2+} и F^- в растворе с 2.7×10^{-6} моль/л Sm^{3+}. Показано, что оптическая плотность раствора, содержащего 10.8×10^{-6} моль/л Sm^{3+}, составляет 0.58 независимо от концентрации Ca^{2+} и F^-.

***Ключевые слова:** самарий, определение, спектрофотометрия в УФ-видимом диапазоне, Арсеназо III.*

Introduction. Samarium is widely used in industrial production, such as cobalt alloys [1–4], luminescent materials [5, 6], ceramic materials [7], permanent magnets [8], and so on. The molten salt electrolysis is a traditional preparation process of the samarium metal and alloys in the previous studies [9–15]. Our group has reported the preparation and characterization of Sm_2Fe_{17} alloy in LiF–CaF_2–SmF_3 and $CaCl_2$–CaF_2–$SmCl_3$ molten salt [16, 17], where the current efficiency in the electrolysis process is difficult to calculate, which is related to the samarium concentration in the molten salt. We have also reported on the preparation and characterization of SmF_3 by solid-solid synthesis (NH_4HF_2 + Sm_2O_3) [18], but the fluorination percentage was hard to determine. With the aim of solving these problems, we paid attention to the sa-

---

marium analysis. There are many methods to determine Sm^{3+} such, as ICP-AES, ICP-MS, XRF, and spectrophotometry [19–23]. Spectrophotometry has many advantages such as fast, sensitive, and simple equipment, and it has been used a lot for qualitative and quantitative analysis [24–28]. The peak intensity at 654 nm was used to analyze lanthanide complexes by a UV-visible spectrometer due to Arsenazo III as a chromophoric indicator without affecting the absorbance peak intensity at this wavelength [29–31]. Kendrick et al. reported that the spectrum of the lanthanide complex with Arsenazo III was grossly and variably affected by Ca^{2+} [32]. Rohwer et al. investigated that the effect of anions on the absorbance increases in the following order: $ClO_4^- < NO_3^- \approx I^- \approx NCS^- < Cl^- << SO_4^{2-} << F^-$ [30]. The concentration of Sm element remaining in the melt can be determined by spectrophotometry. Despite all this, when Ca^{2+} and F^- existed in the samples for analysis, it involved serious interference to identify the concentration of Sm^{3+} by spectrophotometry due to the change in the absorbance, so that an extracting method [33–35] or adding masking agents [36] was used to eliminate the interference, resulting in a complex program of analysis for determining Sm^{3+} concentration.

In this present work, a suitable pH was found to dilute the Arsenazo III-samarium solution, and the effects of Ca^{2+} and F^- on the absorbance were investigated to establish the quantitative relation of the absorbance among Ca^{2+}, F^-, and Sm^{3+} in an aqueous solution to simplify the determination method of UV-visible spectrophotometry.

Experimental. Chemicals used were analytical-grade reagents. Aqueous solutions were prepared using deionized water. The sample was dissolved by hydrochloric acid in a solution adjusted to pH 2.8 with deionized water, then added to the mark in a 100 mL volumetric flask as a buffering solution for investigating spectrophotometric titrations. Because CaF_2-containing samples dissolved poorly, a proper amount of perchloric acid was added to the aqueous solution, and the whole heated at 80°C in a thermostatic water-bath for 2 h, then adjusted to pH 2.8 by sodium hydroxide.

A UV765 UV-vis spectrometer from INESA Analytical Instrument Company was used to measure the absorbance of the analytical solution against deionized water as a reference, where the Lamber–Beer law is as follows:

$$A = \lg(I_0/I_t) = kNC, \qquad (1)$$

where A is the absorbance, I_0 and I_t are the intensities of incident light and transmission light, N and C are the thickness (1.0 cm) and the concentration (g/L) of the solution, and k is the absorbance coefficient.

In this work, Arsenazo III ($C_{22}H_{18}As_2N_4O_{14}S_2$) was used as a chromophoric indicator due to its high sensitivity and low selectivity for the determination of various lanthanides over a wider pH range [37–39].

The maximum absorbance wavelength (λ_{max}) for determining Ca^{2+}, F^-, and Sm^{3+} in the aqueous solution was first measured for improving the determination accuracy. The concentration of Arsenazo III was changed at 6.44×10^{-4}, 12.88×10^{-4}, and 25.76×10^{-4} mol/L in deionized water to prepare the analysis solution, where 3 mL was taken to carry out the UV-vis scan to optimize the chromophoric agent amount. The concentrations of $SmCl_3$ at 2.70×10^{-6}, 6.80×10^{-6}, and 10.8×10^{-6} mol/L were changed in the aqueous solution to prepare the buffering samples for investigating the Sm^{3+} effect, because the measured values obey the Lamber–Beer law (Eq. (1)) with ~ 0–10.8×10^{-6} mol/L of Sm^{3+}[39]. For comparison of the Ca^{2+}, F^-, and Sm^{3+} effects on λ_{max}, 47 mg/L of NaF or $CaCl_2$ was added to the aqueous solution, respectively, with 2.70×10^{-6} mol/L $SmCl_3$ and $SmCl_3$-free to prepare the buffering samples.

The concentration of NaF, $CaCl_2$, or CaF_2 was changed at 10, 24, and 47 mg/L in the aqueous solutions, respectively, with 2.7×10^{-6} mol/L $SmCl_3$ and $SmCl_3$-free to prepare buffering samples to investigate the effects of Ca^{2+} and F^- concentration on the absorbance. Simultaneously, the concentration of Sm^{3+} was changed as 2.7×10^{-6}, 4.1×10^{-6}, 5.4×10^{-6}, 6.8×10^{-6}, 8.1×10^{-6}, 9.4×10^{-6}, and 10.8×10^{-6} mol/L in the aqueous solutions with different mass ratio of $CaCl_2$ to CaF_2 as 0/100, 59/41, 68/32, 77/23, 85/15, 93/7, and 100/0, respectively, while the total amount of $CaCl_2$ and CaF_2 was held constant at 100 mg/L.

Finally, 1 mL Arsenazo III aqueous solution with the concentration of 12.88×10^{-4} mol/L was added into 492-3 of the above buffering solutions to prepare the analytical solutions, which were adjusted to pH 2.8 by hydrochloric acid or sodium hydroxide; 3mL of the analysis solution was taken to carry out the UV-vis scan to study the effects of Sm^{3+}, Ca^{2+}, and F^- concentration on the absorbance.

Results and discussion. The effect of pH on the Arsenazo III-samarium solution was studied from the spectral change of an aqueous solution with 12.88×10^{-4} mol/L Arsenazo III and 2.7×10^{-6} mol/L $SmCl_3$, as a function of pH. The peak at 654 nm reached its maximum at pH 2.8 (Fig. 1a). It was chosen for all samples.

Figures 1b–d show that the wavelength of the maximum absorbance (λ_{max}) changed with Arsenazo III, Sm^{3+}, Ca^{2+}, and F^- concentration in the aqueous solutions. The λ_{max} values for Arsenazo III and Sm^{3+} in the aqueous solutions appeared, respectively, at 534 and 652 nm, and their absorbance values increased with increase in concentration as shown in Fig. 1b,c. The λ_{max} values for Ca^{2+} in the aqueous solutions appeared at 646 nm close to that of Sm^{3+} (the intersection of peak shoulder extension lines), while that of F^- and Na^+ in the aqueous solutions had not appeared as shown in Fig. 1d. Interestingly, the absorbance curves of the Arsenazo III–NaF solutions are the same as that of the Arsenazo III-aqueous solution between wavelengths of 600 and 700 nm. However, the effects of Ca^{2+} and F^- on the absorbance at λ_{max} of Sm^{3+} in the aqueous solutions are obviously different, i.e., increased after addition of Ca^{2+} but decreased after addition of F^- into the aqueous solutions, so the mechanism can be deduced that Ca^{2+} combined with Arsenazo III to form a complex for the absorbance increase, while F^- acts on Sm^{3+} to degrade the complex for the absorbance decrease. The above results can also be confirmed by the absorbance change at λ_{max} of Arsenazo III. The absorbance decreased after addition of Sm^{3+} and Ca^{2+}, while it increased after addition of F^- in the aqueous solutions. This also indicates that the Arsenazo III complex stabilization would be influenced by Sm^{3+}, Ca^{2+}, and F^-. In addition, it was also observed that when the wavelength was close to 700 nm, the effect of the peak from λ_{max} of Arsenazo III on the absorbance at λ_{max} of Sm^{3+} had decreased, so the absorbance at 660 nm was used in this work to study the spectrophotometric behavior for the determination of Sm^{3+} concentration in order to enhance the measurement accuracy.
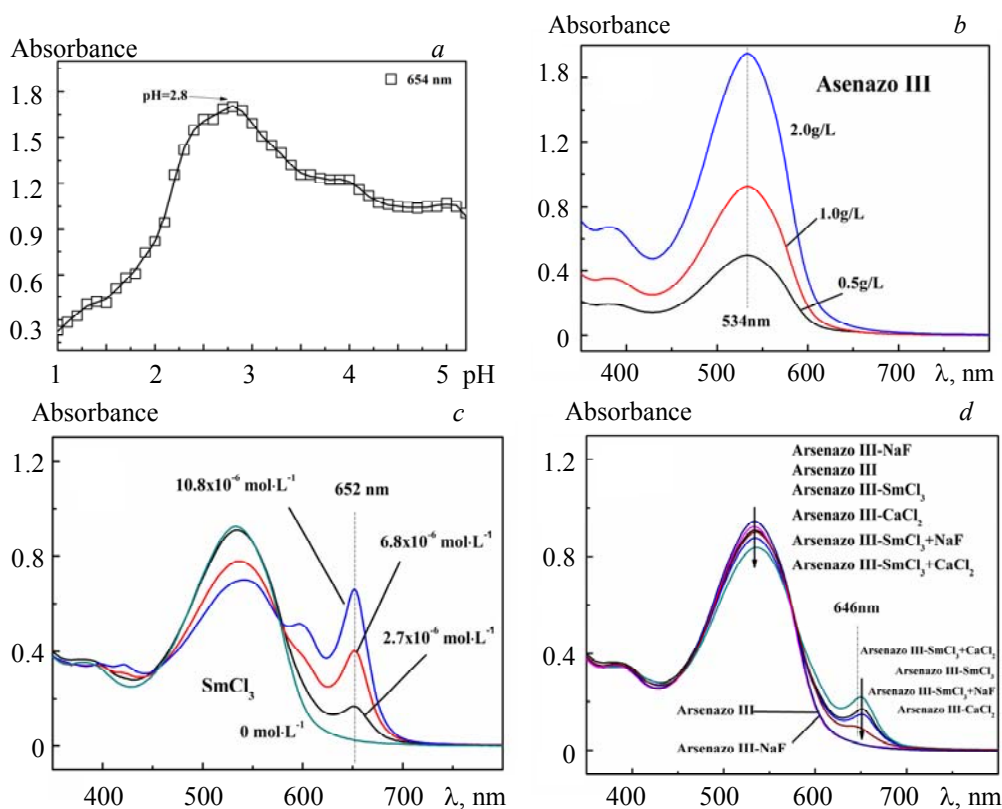

Fig. 1. Dependences of wavelength on absorbance of Arsenazo III, Sm^{3+}, Ca^{2+}, F^- concentration or pH in aqueous solutions: (a) pH vs absorbance of the aqueous solution; (b) effect of Arsenazo III; (c) effect of $SmCl_3$ concentration in the aqueous solution with 12.88×10^{-4} mol/L Arsenazo III; (d) effects of different species (47 mg/L) in the solutions, respectively, with 12.88×10^{-4} mol/L Arsenazo III or 12.88×10^{-4} mol/L Arsenazo III and 2.7×10^{-6} mol/L $SmCl_3$.
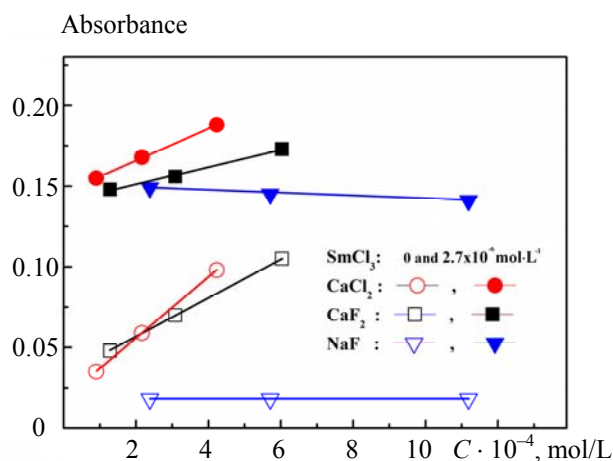
Absorbance

Fig. 2. Dependence of the absorbance at 660 nm on the concentrations of F^-, Ca^{2+}, and both Ca^{2+} and F^- in the aqueous solutions without Sm^{3+} and with 2.7×10^{-6} mol/L Sm^{3+}

Figure 2 shows that the absorbance at 660 nm changed with the concentrations of NaF, $CaCl_2$, and CaF_2 in the aqueous solutions, respectively, without Sm^{3+} and with 2.7×10^{-6} mol/L Sm^{3+}. This clearly shows that the absorbance increased with increase in Ca^{2+} concentration, while it had not changed with increase in F^- concentration in the aqueous solution without Sm^{3+}. However, the absorbance decreased with increase in F^- concentration and increased with increase in Ca^{2+} concentration in the aqueous solution with 2.7×10^{-6} mol/L Sm^{3+}. This shows that the mechanism of Sm^{3+} and Ca^{2+} in enhancing the increase in absorbance is the same but different from that of F^-. The experimental result also shows that the absorbance after additions of Ca^{2+} and F^- (CaF_2) simultaneously into the aqueous solution is smaller than that after addition of Ca^{2+} ($CaCl_2$) only into the aqueous solution.

The absorbance of the aqueous solutions with different concentrations of Sm^{3+}, Ca^{2+}, and F^- is listed in Table 1 and plotted in Fig. 3. They show that the absorbance of the aqueous solutions increases linearly with increase in Sm^{3+} concentration, greater than that of Ca^{2+} concentrations, which result in decreases in Ca^{2+} and F^- effects on the absorbance with increase in Sm^{3+} concentration, so that both effects can be ignored at $C(Sm^{3+}) = 10.8 \times 10^{-6}$ mol/L. The relationships between the absorbance and Sm^{3+} concentration at two different concentration ratios of $CaCl_2$ to CaF_2 consist of an absorbance triangle together with the relationship between the absorbance and the different concentration ratios at 2.70×10^{-6} mol/L of Sm^{3+} concentration.
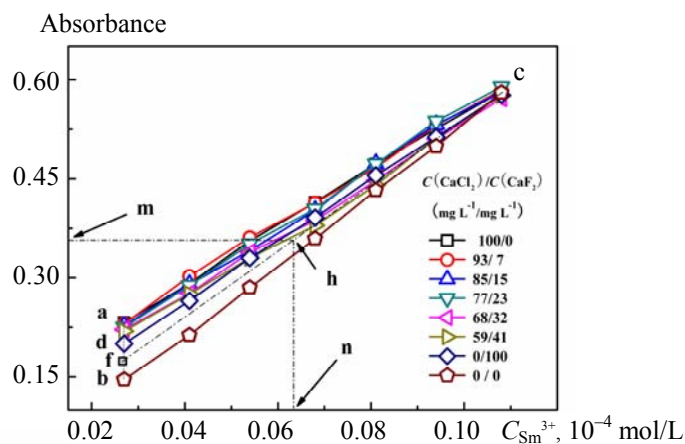
Absorbance

Fig. 3. Effect of $CaCl_2$ to CaF_2 mass ratio on the absorbance of the aqueous solutions with different Sm^{3+} concentrations.

TABLE 1. Absorbance of Aqueous Solutions Measured at Different Concentrations of Sm^{3+}, Ca^{2+}, and F^-

C_{CaCl_2}/C_{CaF_2}, mg/L	Ca^{2+}, 10^{-3} mol/L	F^-, 10^{-3} mol/L	C (Sm^{3+}), 10^{-6} mol/L						
			2.7	4.1	5.4	6.8	8.1	9.4	10.8
100/0	0.901	0	0.232	0.291	0.356	0.414	0.472	0.526	0.582
93/7	0.928	0.180	0.230	0.300	0.361	0.413	0.467	0.531	0.584
85/15	0.958	0.384	0.227	0.290	0.341	0.402	0.473	0.532	0.581
77/23	0.989	0.590	0.225	0.288	0.351	0.404	0.472	0.537	0.589
68/32	1.023	0.820	0.222	0.276	0.338	0.387	0.447	0.510	0.571
59/41	1.058	1.052	0.219	0.275	0.330	0.379	0.446	0.512	0.576
0/100	1.282	2.564	0.200	0.265	0.330	0.391	0.455	0.513	0.577
0/0	0	0	0.146	0.213	0.285	0.359	0.432	0.499	0.580

It is supposed that the effect of Ca^{2+} or F^- concentration on the absorbance has a linear relationship according to the above result, as shown in Fig. 2. We can obtain a quantitative relationship of the absorbance of the aqueous solutions with different concentrations of Ca^{2+} and F^- at 2.70×10^{-6} mol/L Sm^{3+} as follows:

$$A = 0.146 + k_{Ca}C(Ca^{2+}) + k_F C(F^-), \tag{2}$$

where A is the absorbance value of the aqueous solution; k_{Ca} and k_F are effect factors of Ca^{2+} and F^- respectively to the absorbance,

$$C(Ca^{2+}) = (A - 0.146)/k_{Ca} - k_F C(F^-)/k_{Ca}. \tag{3}$$

The $C(Ca^{2+})$ and $C(F^-)$ dependences of the absorbance at 2.70×10^{-6} mol/L of the Sm^{3+} concentration are shown in Table 1 and plotted in Fig. 4a. Though k_{Ca} and k_F were constant in Fig. 2 for a single component of Ca^{2+} or F^-, the real values changed with the ratio of $C(F^-)$ to $C(Ca^{2+})$ as shown in Fig. 4b. This shows that Ca^{2+} and F^- have interacted.

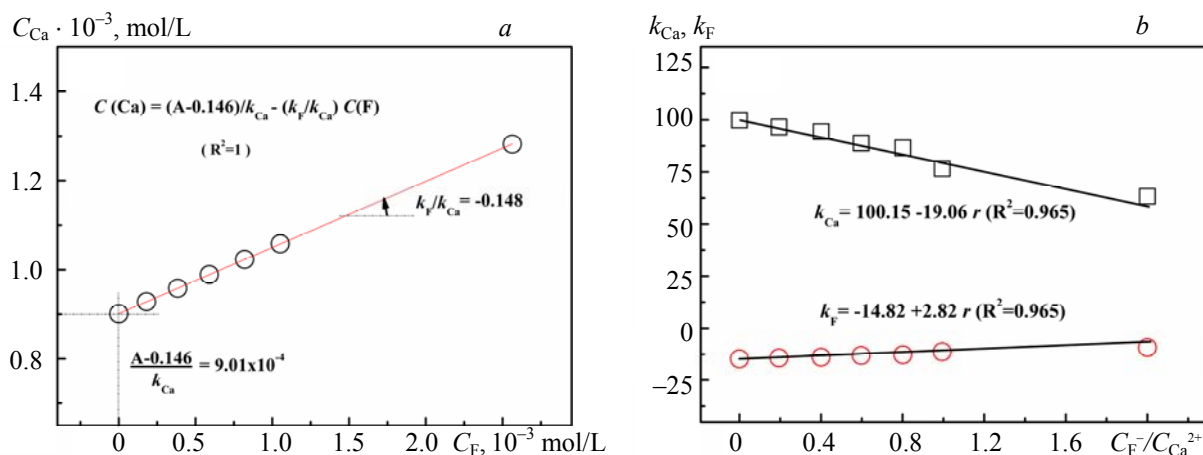Fig. 4. Relationship between $C(Ca^{2+})$ and $C(F^-)$ concentrations (a), changes of k_{Ca} and k_F with the ratio of $C(F^-)$ to $C(Ca^{2+})$ (b) at 2.70×10^{-6} mol/L of Sm^{3+} concentration.

Furthermore, k_{Ca} and k_F were substituted into Eq. (2) as variables, and the quantitative relationship between the absorbance and the concentrations of $C(F^-)$ to $C(Ca^{2+})$ was obtained at 2.70×10^{-6} mol/L of Sm^{3+} concentration as follows:

$$A = 0.146 + 97.23 \cdot C(Ca^{2+}) - (32.25 - 2.64r) \cdot C(F^-), \tag{4}$$

where r is the concentration ratio of $C(F^-)$ to $C(Ca^{2+})$.

According to Eq. (2) it can be deduced that the absorbance should be extended to 0.146 at "b" point in Fig. 3 (corresponding to the absorbance of the aqueous solution without Ca^{2+} and F^-). The absorbance triangle is formed by the three sides of ab, bc, and ac, in which the absorbance of a and b points can be calculated to be 0.234 and 0.146 by Eq. (2), and the absorbance at c is 0.580 at 10.8×10^{-6} mol/L of Sm^{3+} concentration

as showed in Fig. 3. Then the quantitative relationship between the absorbance and the Sm^{3+} concentration on ac and bc can be obtained as follows:

$$\text{For } ac, \text{ A} = 0.118 + 42765 \cdot C(Sm^{3+}), \tag{5}$$

$$\text{For } bc, \text{ A} = 0.001 + 53581 \cdot C(Sm^{3+}). \tag{6}$$

On the contrary, when the concentrations of Ca^{2+} and F^- in the Sm^{3+}-containing aqueous solution are known, the absorbance at 2.70×10^{-6} mol/L of Sm^{3+} concentration is calculated by Eq. (4). Then a linear equation of the quantitative relationship between the absorbance and Sm^{3+} concentration such as Eq. (5) or (6) is obtained with the absorbance 0.580 at 10.8×10^{-6} mol/L of Sm^{3+} concentration. So, if the absorbance of the Sm^{3+}-containing aqueous solution is measured by UV-vis spectrometry, it can be combined with the linear equation to obtain a certain concentration of Sm^{3+} in the solution. For example, according to the concentrations of Ca^{2+} and F^- in the Sm^{3+}-containing aqueous solution, the absorbance (f) at 2.70×10^{-6} mol/L of Sm^{3+} concentration is calculated by Eq. (4), and a linear equation (for the fc line) of the quantitative relationship between the absorbance and the Sm^{3+} concentration such as Eq. (5) or (6) is obtained, in which the absorbance (c) is 0.580 at 10.8×10^{-6} mol/L of Sm^{3+} concentration. Moreover, the absorbance (m) of the Sm^{3+}-containing solution is measured by UV-vis spectrometry. It is combined with the linear equation of the "h" point to obtain the concentration (n) of Sm^{3+} in the solution.

The above result shows that the method can be used to detect the concentration of Sm^{3+} in the aqueous solution containing Ca^{2+}, F^-, or both of Ca^{2+} and F^- in the range of Sm^{3+} concentration from 2.7×10^{-6} to 10.8×10^{-6} mol/L. The maximum deviation of the experimental values was found to be $\pm 0.49 \times 10^{-6}$ mol/L as shown in Table 2, and the relative error is not larger than 7.2%. Therefore, this is a potential method to detect the concentration of Sm^{3+} in molten salts containing Sm^{3+} such as $SmCl_3$–$CaCl_2$, $SmCl_3$–CaF_2, or $SmCl_3$–$CaCl_2$–CaF_2 for extraction of rare earth metals.

TABLE 2. Error Analysis for the Detection of Sm^{3+} in the Solution Containing Ca^{2+} and F^-

$C(Sm^{3+})$ added		4.1×10^{-6} mol/L		6.8×10^{-6} mol/L		9.4×10^{-6} mol/L		
Ca^{2+}, 10^{-3} mol/L	F^-, 10^{-3} mol/L	Detection values						$C(Sm^{3+})=f[A]*$
		A	$C(Sm^{3+})$, 10^{-6} mol/L	A	$C(Sm^{3+})$, 10^{-6} mol/L	A	$C(Sm^{3+})$, 10^{-6} mol/L	
0.901	0	0.291	4.04	0.414	6.92	0.526	9.54	$C=2.338 \times 10^{-5}(A - 0.118)$
0.928	0.180	0.300	4.31	0.413	6.93	0.531	9.67	$C=2.318 \times 10^{-5}(A - 0.114)$
0.958	0.384	0.290	4.13	0.402	6.70	0.532	9.69	$C=2.296 \times 10^{-5}(A - 0.110)$
0.989	0.590	0.288	4.17	0.404	6.81	0.537	9.83	$C=2.276 \times 10^{-5}(A - 0.105)$
1.023	0.820	0.276	3.95	0.387	6.45	0.510	9.22	$C=2.255 \times 10^{-5}(A - 0.101)$
1.058	1.052	0.275	3.98	0.379	6.31	0.512	9.28	$C=2.236 \times 10^{-5}(A - 0.097)$
1.282	2.564	0.265	4.07	0.391	6.76	0.513	9.37	$C=2.140 \times 10^{-5}(A - 0.075)$
1.282	8.715	0.213	3.96	0.359	6.68	0.499	9.29	$C=1.866 \times 10^{-5}(A - 0.001)$
Max. deviation		± 0.21		± 0.49		± 0.43		

* This was obtained by the absorbance in aqueous solutions with 2.7×10^{-6} and 10.8×10^{-6} mol/L of Sm^{3+}.

Conclusion. The influences of Na^+, Cl^-, Ca^{2+}, and F^- on the absorbance of solutions with different Sm^{3+} concentrations and the quantitative relationship were investigated by UV-vis spectrophotometry with Arsenazo III. The suitable wavelength of the absorbing peak for the detection of Sm^{3+} concentration in the aqueous solution is 660 nm, in which Na^+ and Cl^- have no influence on the absorbance in the absence of Sm^{3+}. F^- also does not influence the absorbance of the solution without Sm^{3+}, but the absorbance of the solution with Sm^{3+} decreases with increase in F^- concentration and increases significantly with increase in Ca^{2+} concentration. A quantitative relationship for the influence of Ca^{2+} and F^- concentration on the absorbance of solution with $C(Sm^{3+}) = 2.7 \times 10^{-6}$ mol/L was obtained. The influence of Sm^{3+} on the absorbance of the solution is remarkable compared with that of Ca^{2+} and F^-. With increase in Sm^{3+} concentration, the absorbance increases linearly, but the influence of Ca^{2+} and F^- concentration on the absorbance of the solution decreases and can be ignored at $C(Sm^{3+}) = 10.8 \times 10^{-6}$ mol/L. The quantitative relationship between the absorbance of solution and Ca^{2+}, F^-, and Sm^{3+} concentrations was obtained for the detection of Sm^{3+} concentration by

UV-vis spectrophotometry when Ca^{2+}, F^-, or Ca^{2+} and F^- existed in the aqueous solution. Its relative error was not larger than 7.2%.

REFERENCES

1. Z. Q. Xue, L. Liu, Z. Liu, M. Li, D. Lee, R. J. Chen, Y. Q. Guo, A. R. Yan, *Scr. Mater.*, **113**, 226–230 (2016).

2. W. Sun, M. G. Zhu, Y. K. Fang, Z. Y. Liu, H. S. Chen, Z. H. Guo, W. Li, *J. Magn. Magn. Mater.*, **378**, 214–216 (2015).

3. M. Kuru, O. Sahin, S. Ozarslan, A. E. Ozmetin, *J. Alloy. Compd.*, **694**, 726–732 (2017).

4. R. K. Singh, S. V. Kamat, R. P. Mathur, *J. Magn. Magn. Mater.*, **379**, 300–304 (2015).

5. V. I. Kushnirenko, M. V. Sopinskyy, E. G. Manoilov, V. S. Khomchenko, *J. Alloy. Compd.*, **451**, 209–211 (2008).

6. H. Hakala, P. Liitti, K. Puukka, J. Peuralahti, K. Loman, J. Karvinen, P. Ollikka, A. Ylikoski, V. M. Mukkala, J. Hovinen, *Inorg. Chem. Commun.*, **5**, 1059–1062 (2002).

7. J. D. Castillo, A. C. Yanes, S. Abe, P. F. Smet, *J. Alloy. Compd.*, **635**, 136–141 (2015).

8. T. Saito, H. Kitazima, *J. Magn. Magn. Mater.*, **32**, 2154–2157 (2011).

9. G. Cordoba, C. Caravaca, *J. Electroanal. Chem.*, **572**, 145–151 (2004).

10. T. Iida, T. Nohira, Y. Ito, *Electrochim. Acta*, **48**, 2517–2521 (2003).

11. T. Iida, T. Nohira, Y. Ito, *Electrochim. Acta*, **46**, 2537–2544 (2001).

12. T. Iida, T. Nohira, Y. Ito, *Electrochim. Acta*, **48**, 901–906 (2003).

13. L. Massot, P. Chamelot, P. Taxil, *Electrochim. Acta*, **50**, 5510–5517 (2005).

14. Y. H. Liu, Y. D. Yan, M. L. Zhang, J. N. Zheng, Y. Zhao, P. Wang, T. Q. Yin, X. Y. Jing, W. Han, *Electrochim. Acta*, **163**, D672–D681 (2016).

15. Y. H. Liu, Y. D. Yan, M. L. Zhang, Y. Liang, J. M. Qu, P. Li, D. B. Ji, Y. Xue, X. Y. Jing, W. Han, *Electrochim. Acta*, **249**, 278–289 (2017).

16. Q. C. Yan, X. M. Guo. *J. Alloy. Compd.*, **747**, 994–1001 (2018).

17. X. M. Guo, Q. C. Yan, China Patent CN201610183598.1 (2016).

18. Q. C. Yan, X. M. Guo, *Solid State Commun.*, **272**, 63–66 (2018).

19. R. Schramm, *Phys. Sci. Rev.*, **1**, 1–17 (2016).

20. L. O. Dubenskaya, G. D. Levitskaya, N. P. Poperechnaya, *J. Anal. Chem.*, **60**, 304–309 (2005).

21. É. Biémont, *Recent Phys. Scr.*, **119**, 55–60 (2005).

22. H. Kunzendorf, H. A. Wollenberg, *Nucl. Instrum. Methods*, **87**, 197–203 (1970).

23. E. Woznicka, M. Kopacz, M. Umbreit, J. Klos, *J. Inorg. Biochem.*, **101**, 774–782 (2007).

24. N. T. Birgani, S. Elhami, *J. AOAC Int.*, **100**, 224–229 (2017).

25. B. Debus, M. Sliwa, H. Miyasaka, J. Abe, C. Ruckebusch, *Chemometr. Intell. Lab.*, **128**, 101–110 (2013).

26. T. I. Shabatina, A. V. Vlasov, E. V. Vovk, D. J. Stufkens, G. B. Sergeev, *Spectrochim. Acta A*, **56**, 2539–2543 (2000).

27. M. B. Kime, D. Makgoale, *Chem. Eng.Commun.*, **203**, 1648–1655 (2016).

28. N. H. Choi, S. K. Kwon, H. Kim, *J. Electrochem. Soc.*, **160**, A973–A979 (2013).

29. H. Rohwer, E. Hosten, *Anal. Chim. Acta*, **339**, 271–277 (1997).

30. H. Rohwer, N. Collier, E. Hosten, *Anal. Chim. Acta*, **314**, 219–223 (1995).

31. B. Buděšínský, *Collect. Czech. Chem. Commun.*, **28**, 1858–1866 (1963).

32. N. C. Kendrick, *Anal. Biochem.*, **76**, 487–501 (1976).

33. R. Borissova, E. Mitropolitska, *Talanta*, **24**, 49–51 (1979).

34. L. F. Qiu, X. H. Kang, T. S. Wang, *Sep. Sci. Technol.*, **11**, 32–35 (1991).

35. M. D'Orazio, S. Tonarini, *Anal. Chim. Acta*, **351**, 325–335 (1997).

36. Y. J. Dong, K. Gai, X. X. Gong, *J. Chongqing Normal Un-ty (Nat. Sci. Ed.)*, **21**, 43–45 (2004).

37. Y. L. Shi, E. Edward, E. R. Van, *J. Chem. Soc. Dalton Trans.*, 967–974 (1998).

38. K. Matharu, S. K. Mittal, S. K. A. Kumar, *Spectrochim. Acta A*, **145**, 165–175 (2015).

39. X. Z. Yang, *Hydrometallurgy China*, **26**, 109–112 (2007).