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Research Article

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Determination of In^{3+} in solution by ICP-OES and 5-Br-PADAP spectrophotometry

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ABSTRACT

ICP-OES and 5-Br-PADAP spectrophotometry are commonly used in determination of In3+ in solution. In this study, the linear range, detection limit, precision, recovery and the application effects of ICP-OES and 5-Br-PADAP spectrophotometry on determination of In3+ were investigated. The results showed that The results showed that the detection operation of ICP-OES was easier and more convenient in comparison with 5-Br-PADAP. By ICP-OES analysis, wide detection linear range and low the detection limit were obtained. In addition, the detection RSD value of ICP-OES was smaller, meaning the good agreement between determined values and certified values. As a result, ICP-OES was more suitable for determination of In3+ in solution than 5-Br-PADAP spectrophotometry.

Keywords: ICP-OES, 5-Br-PADAP Spectrophotometry, Indium

INTRODUCTION

There are several determination methods of trace In^{3+} in solution, such as spectrophotometry, atomic absorption spectrometry, atomic emission spectrometry and polarography [1]. Among these methods, spectrophotometry is the most widely used one because of simple structure of instrument, low cost, and simple operation [2]. Inductively coupled plasma optical emission spectrometry (ICP-OES) is a well-established multielement technique. In recent years, with the continuous wavelength range and wide detection range, ICP-OES has been widely employed in geology, environmental protection, chemical engineering, biology, pharmaceutics, food, metallurgy and agriculture[3~4].

EXPERIMENTAL SECTION

2.1 5-Br-PADAP Spectrophotometry

2.1.1 Instruments and reagents

Main instruments 752P Uv-vis spectrophotometer- (Shanghai Olympic Doppler Instrument Co., LTD), pHS-25 Magnetic digital acidometer (Shanghai Branch precision instruments Co., LTD), AR2140 Electronic balance (Shanghai Mettler Toledo instrument Co., LTD), 100~1000 μL and 20~200 μL sampler (Black & Decker Finland laboratory equipment(China) Co., Ltd).

Main reagents Indium sulfate (AR), Indium standard solution (national standard samples, the GSB 04-1731-20041000 $g{\cdot}L^{-1}$, national non-ferrous metals and electronic materials analysis and testing center), 5-Br-PADAP ethanol solution(0.05%), NaAc-HAc buffer solution(pH=4.70), Anhydrous ethanol(AR). Deionized water was used through all experiments.

2.1.2 Detection principle

There are mainly three spectrophotometry methods for indium detection, such as triphenylmethane dye spectrophotometry, azo photometry and fluorone photometric method. The method of 2-(5-bromo-2-pyridylazo)-

5-diethylaminophenol (5-Br-PADAP) spectrophotometry was adopted in our experiment. Under certain conditions, indium ions can complexate with 5-Br-PADAP to form an orange binary complex. The complex compound has strong absorption at 565 nm [5].

2.1.3 Experimental Procedure

A solution of $In_2(SO_4)_3$ with a desired concentration was carefully prepared, then diluted to certain multiple before use. The accurate volume of solution of $In_2(SO_4)_3$ was placed into a colorimetric tube(10 mL), and mixed with anhydrous ethanol(2 mL), NaAc-HAc buffer solution(2 mL, pH=4.7) and 5-Br-PADAP ethanol solution(0.4 mL, 0.05%) in order. The mixture was diluted to the mark with deionized water and shaked thoroughly. With the reagent blank as reference and 1 cm cuvette, the absorbance was detected at 565 nm[6~7].

Standard curve: 0, 0.2, 0.4, 0.6, 0.8, 1.0 mL 5 mg·L^{-1} indium standard solution was respectively placed in 10 mL colorimetric tube. Then the absorbance was detected by the above method. The standard curve of indium was prepared with concentration and absorbency.

2.2 ICP-OES

2.2.1 Instruments and Reagents

Main instruments Inductively coupled plasma optical emission spectrometer (Perkin Elmer OPTIMA 7000DV), Electronic balance AR2140 (Shanghai Mettler Toledo instrument Co, LTD), 100~1000 μL and 20~200 μL sampler (Black &Decker Finland laboratory equipment (China) Co., Ltd).

Main reagents Indium sulfate (AR), Indium standard solution (national standard samples, the GSB 04-1731-2004, 1000 μg·mL^{-1}, national non-ferrous metals and electronic materials analysis and testing center)

1.2.2 Working Conditions

The ICP-OES operating conditions were listed in Tab.1

Tab.1 working parameters of ICP-OES

Sample uptake rate /(mL·min^{-1})	Nebulizer gas /(L·min^{-1})	Power /(W)	Outer gas /(L·min^{-1})	Intermediate gas /(L·min^{-1})
1.50	0.2	1300	15	0.80

2.2.3 Experimental Procedure

The background wavelength corrections were performed manually at appropriate background positions for each analyte peak. The best analytical wavelength of indium was fixed as 325.609 nm. The detection was operated under the conditions described in Tab.1.

Standard curve: 0, 10, 50,100, 200, 400 μL indium standard solution(1000 μg·mL^{-1}) was respectively placed in 10 mL colorimetric tube. The solution was diluted to the mark with deionized water and shaked well. Then the detection was operated under the conditions of tab.1.

RESULTS AND DISCUSSION

3.1 Linear range

By 5-Br-PADAP spectrophotometry, the regression equation of indium standard curve was y=0.705x+0.0102. The corresponding coefficient (R^2) was 0.9992. In the range of 0~500 μg·L^{-1}, the standard concentration and absorbance values showed a good linear relationship. By ICP-OES, the indium standard curve regression equation was y=0.9875x+0.0654. The correlation coefficient (R^2) was 1. The standard concentration and measured values showed a good linear relationship in the range of 0~20000 μg·L^{-1}. As a result, the ICP-OES method was better than the 5-Br-PADAP spectrophotometry, due to the wider linear range and the better linear relationships between measured value and standard value. The ICP-OES method could be directly used to determine the sample with relatively the high concentration of indium species in a simple manner.

3.2 Detection limit

According to the calculation method of IUPAC, the limits of detection (LOD) were calculated from the standard deviation (3σ) of ten measurements of the blank solution and slope ratio. As measurement results showed, the indium detection limit of 5-Br-PADAP spectrophotometry was 0.028 mg·L^{-1}, while the detection limit of ICP-OES is 0.015 mg·L^{-1}. The detection limit of ICP-OES method is nearly half of that of the 5-Br-PADAP spectrophotometry. So the sensitivity of ICP-OES method is better.

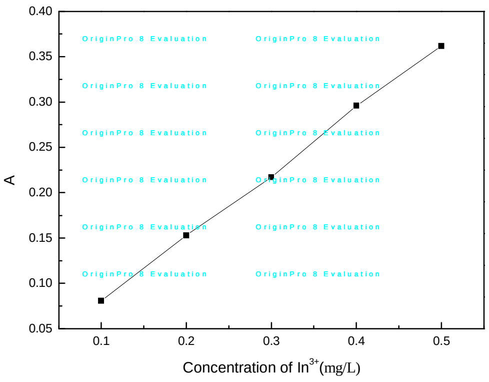

Fig.1 standard curve of 5-Br-PADAP spectrophotometry

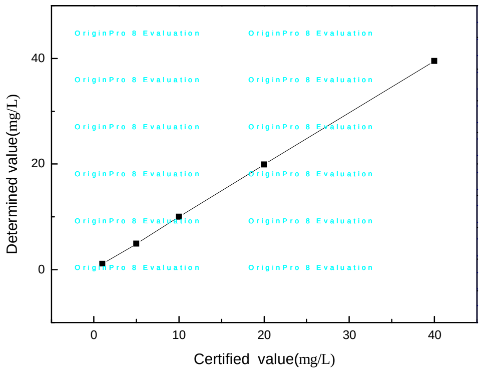

Fig.2 Standard curve of ICP-OES

3.3 Comparison of precision

Via the 5-Br-PADAP spectrophotometry and ICP-OES, 5 groups of solution sample were parallelly determined for 6 times. Then the determined values were averaged and the relative standard deviation (RSD) of each sample by both methods were calculated, respectively. The results were summarized in Tab.2.

Tab.2 the accuracy test results of 5-Br-PADAP spectrophotometry and ICP-OES

sample	5-Br-PADAP spectrophotometry		ICP-OES	
	Determined value (mg·L^{-1})	RSD (%)	Determined value (mg·L^{-1})	RSD (%)
1	7.49	5.83	7.33	2.15
2	9.26	2.84	9.19	0.89
3	10.23	4.05	10.67	1.14
4	2.96	5.58	2.41	1.94
5	5.69	5.35	5.30	0.81

The precision of method was evaluated as the relative standard deviation obtained by testing 5 groups sample for 6 times. As shown in Tab.2, considering 6 replicates of 5 groups sample submitted to ICP-OES, the RSD was below 2.15%, indicating good repeatability. And considering five replicates of sample submitted to 5-Br-PADAP spectrophotometry, the RSD ranged from 2.5% to 6%, obviously higher than that of ICP-OES. Therefore, the 5-Br-PADAP spectrophotometry with poor reproducibility was less reliable than ICP-OES.

Tab.3 Recovery results for In^{3+} by 5-Br-PADAP spectrophotometry

Sample	Original value /(mg·L^{-1})	Standard Added /(mg·L^{-1})	Determined value /(mg·L^{-1})	Recovery (%)
1	7.49	20	26.6	95.6
2	9.26	20	28.57	96.6
3	10.23	20	29.35	95.6
4	2.96	20	22.45	97.5
5	5.69	20	25.08	96.9

3.4 Comparison of recovery

Recoveries was necessary in order to estimate the accuracy and precision of determination methodology. According to the standard addition method, 5 groups of solution sample were parallelly determined by both 5-Br-PADAP spectrophotometry and ICP-OES for 6 times. The recovery was calculated based upon the detection results, and were collected in Tab.3 and Tab.4 .

Tab.4 Recovery results for In^{3+} by ICP-OES

Sample	Original value /(mg·L^{-1})	Standard Added /(mg·L^{-1})	Determined value /(mg·L^{-1})	Recovery /(%)
1	7.33	20	27.02	98.5
2	9.19	20	29.77	102.9
3	10.6	20	30.98	101.6
4	72.4	20	22.65	101.2
5	15.30	20	24.9	98.0

As can be seen in Tab.3 and Tab.4, indium determination recovery of 5-Br-PADAP spectrophotometry ranged from 95.5% to 97.5%. Comparing with the ture value, the result was lower with a large error. The indium determination recovery of ICP-OES ranged from 98% to 103%, closer to real value.

3.5 Application examples

Micro and traces of In^{3+} can be enriched on the amino chelating fiber, and then be eluted by a certain amount of sulfuric acid. The elution was diluted to 0~500 μg·L^{-1}, determined by the method of 5-Br-PADAP spectrophotometry. Based on the standard curves of In^{3+}, the indium elution curve was produced between In^{3+} concentration and elution volume, which was shown in Fig.3. At the same time the corresponding samples was determined by the method of ICP-OES. And the elution curve was shown in Fig.4.

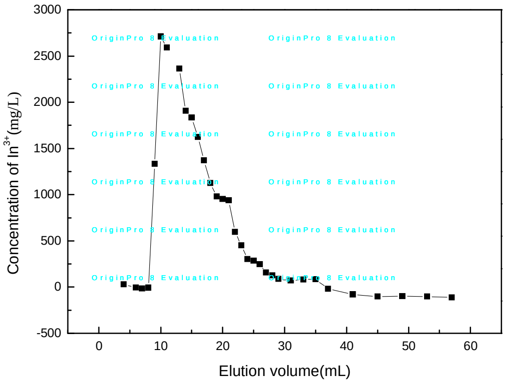

Fig.3 Elution curve of In^{3+} by 5-Br-PADAP spectrophotometry

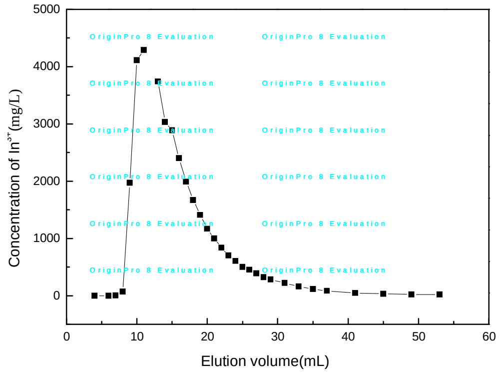

Fig.4 Elution curve of In^{3+} by ICP-OES

Seen from Fig.3 and Fig.4, the indium elution curve by 5- Br-PADAP spectrophotometry and ICP-OES was similar in the shape, and consistent with the desorption rules. But the indium elution curve of ICP-OES was smoother and neater in the shape than that of 5-Br-PADAP spectrophotometriy, which is possibly due to the poor stability of complex formed in spectrophotometry method and the poor stability of spectrophotometer. The biggest difference between Fig.3 and Fig.4 was that concentration value of indium by ICP-OES was significantly higher than that of 5-Br-PADAP spectrophotometry. This was in agreement with the previous research results. The possible reason was the narrow detecting range of 5-Br-PADAP spectrophotometry. Thus, the high concentration of the sample must be diluted repeatedly for several times before determination.

CONCLUSION

Through comparing the method of 5-Br-PADAP spectrophotometry with ICP-OES in the operation, linear range, detection limit, precision, recovery and the actual application effect, we found that in the 5-Br-PADAP spectrophotometric method, the stability of complex was poor, the reagents used in the color reaction were large, and the operation process was complicated. However regarding ICP-OES, without color reaction, the operation was more simple. With wider linear detection range, the high concentration of the sample could be directly introduced into the ICP-OES without any dilution of the sample and with no pollution of sample. ICP-OES presented lower detection limit, better precision and higher detection accuracy. So ICP-OES was simpler, stable and reliable. In short, ICP-OES method was superior to 5-Br-PADAP spectrophotometry from several aspects. But for the high cost of instrument, the use of ICP-OES method was limited. However the instrument of spectrophotometry was simple, with lower operating cost, so it was more widely used, especially in small enterprises and routine laboratory testing. In the future, spectrophotometry also requires to improve the sensitivity and selectivity of color reaction, especially in multicomponent complex system. It also need to be improved the anti-interference ability and accuracy of the method, in order to directly determine indium in the aqueous phase. We should find techniques of more effective separation and enrichment, and develop better selective and more sensitive detection method. Nowadays the most active and promising aspect of spectrophotometry is application of chemometric methods and computer programming analysis of absorption spectrum to realize multicomponent simultaneous determination.

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