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Study on Atomic Fluorescence Spectrometry Excited by Synchrotron Radiation

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A novel analysis approach using atomic fluorescence excited by synchrotron radiation is presented. A system for synchrotron radiation-atomic fluorescence spectrometry is developed, and experimental conditions such as flow rate, analyte acidity, concentration of pre-reducing and hydrogenation system are optimized. The proposed method is successfully applied to get an excitation spectrum of arsenic. Seven of ten primary spectral lines, four of which have never been reported by means of atomic fluorescence spectrometry, agree well with the existing reports. The other three are proposed for the first time. Excitation potentials and possible transitions are investigated. Especially for the prominent line at 234.99 nm, the mechanism of generation is discussed and a model of energy transition processes is proposed.

Key words: Synchrotron radiation, Atomic fluorescence, Arsenic, Energy transition

I. INTRODUCTION

Atomic fluorescence spectrometry (AFS) is a traditional and effective technique for investigation of atomic energy levels and determination of trace elements, owing to its brief spectral lines, little disturbance, high sensitivity, and good precision [1]. The elements all have their characteristic sensitive spectral lines and the strength of the fluorescence signal produced is proportional to the intensity of the incident radiation before saturation. Consequently, the development of tunable and high power output excitation source tends to be of more significance.

At present, high-intensity hollow cathode lamps (HCLs) are widely used for AFS [2-4]. But they all radiate a fixed wavelength of light, according to the atoms to be analyzed, so they cannot be used for investigation of atomic energy levels. Lasers with their advantages in intensity, orientation, and monochromaticity, have also been tried for atomic fluorescence analysis [5-7]. However, the wavelength output of existent dye lasers is beyond the sensitive wavelengths of most elements. Moreover, the tunable wavelength range of single dye laser is too narrow to detect atomic energy levels [8,9]. In recent years considerable efforts have been put into the applications of AFS and there are few reports that focus on theoretic studies on atomic excitation spectral lines, energy transitions, and novel excitation sources.

In a synchrotron, electrons travelling at speeds that approach the speed of light are made to travel in near-circular paths by using powerful magnets, which causes

a range of wavelengths to emit so-called synchrotron radiation (SR) [10]. The wide wavelength range of SR, from hard X-ray and soft X-ray to vacuum ultraviolet, visible light and infrared regions, makes it be useful in basic science, energy sources, material, and environment science [11-14]. SR has been introduced in photoionization and studies on energy transition [15-17]. Also, extensive use of SR in X-ray fluorescence (SR-XRF) [18-20] and extended X-ray absorption of fine structure (EX-AFS) for structural analysis [21-23] is well known. With limited equipment popularity, few scientists have applied synchrotron radiation in the field of atomic spectrometry.

Arsenic is one of the ubiquitous toxic trace elements, representing a major toxicological and environmental concern, and for this reason, considerable efforts have been made in developing sensitive methods for its detection [24-26]. The most popular and traditional methods for the determination of arsenic are atomic absorption spectrometry or atomic fluorescence spectrometry, in which hydride generation (HG) is usually employed [27-29]. Arsenic atoms have complicated spectral lines, but only a few of them are used for detection. As one way of reducing the limit of detection, a more sensitive spectral line can be chosen. Before that can be done, it is apparent that the spectral lines of arsenic atoms must be investigated.

In this work, the synchrotron radiation was theoretically and practically studied as a new source for atomic fluorescence spectrometry. A device for synchrotron radiation-atomic fluorescence spectrometry (SR-AFS) is proposed. Ten excitation spectral lines of arsenic, excited by synchrotron radiation in wavelength scanning, are detected. Seven of them, four of which had never been reported by means of atomic fluorescence spectrometry, agree well with previous literature. The

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other three are proposed for the first time, and the energy transitions are confirmed. Excitation potentials and possible transitions are investigated. Especially for the prominent line at 234.99 nm, the mechanism of generation is discussed and a model of energy transition processes is proposed.

II. EXPERIMENTS

A. Apparatus

Equipment included high flux vacuum ultraviolet and ultraviolet beamline (focula dimension of 2 mm×1 mm, scan wavelength was 190-250 nm. National Synchrotron Radiation Laboratory, University of Science and Technology of China); Hamamatsu H6420 photon counter (Hamamatsu Photonics K.K., Japan); and IFIS-C peristaltic pumps (Xi'an Ruimai Electronic Technology Co., Ltd., Xi'an, China); A home-made quartz tube (7 mm i.d.×14 mm length, combination of two layers homocentric circle of quartz, between the two layers were electric cooker wool to heat the atoms to gaseous atoms) was used as the atomizer.

The device of combination of synchrotron radiation and atomic fluorescence spectrometry for element analysis is shown in Fig.1.

Synchrotron radiation light radiated to the refocus mirror through the grating, then went into exit slit after focusing, and finally got above atomizer via an aperture. The fluorescence signal generated by excited gaseous atoms was measured by a photo multiplier tube (PMT), and the signal was imported to the computer (the signal was handled by a program offered by the National Synchrotron Radiation Laboratory). To prevent disturbance from light source, PMT was installed perpendicular to the light source. Similarly to prevent disturbance from surroundings, the atomizer and PMT were put in a black box, and synchrotron radiation light got to gaseous atoms via the aperture.

The schematic diagram of the generation of atomic

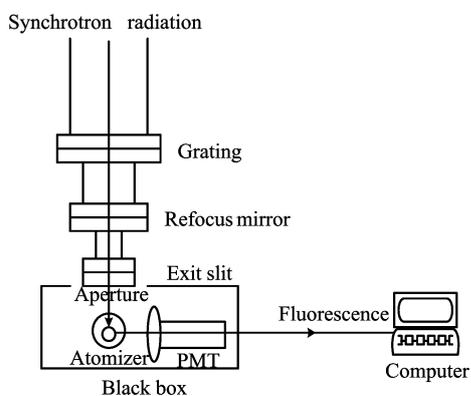


FIG. 1 Schematic diagram of SR-AFS installation.

fluorescence is shown in Fig.2.

Gaseous atoms were produced by hydride generation. The analyte and KBH_4 solution went through peristaltic pumps, and got to a home-made four-way valve of polytetrafluoroethylene (PTFE) driven by carrier gas, then entered a home-made gas-liquid separator after sufficient mixing and reaction. The gaseous hydride in the separator went to a quartz tube atomizer and burnt to gaseous atoms in hydrogen-air flame, protected by the shield gas. Simultaneously, the liquid waste was taken out of the separator by peristaltic pumps. The entire process was automatic and sequential.

B. Reagents and preparation

All reagents were of highest available purity, and of at least analytical grade. Doubly deionized water (DDW) was used throughout.

Stock solutions (1.000 g/L) of arsenic were prepared by dissolving As_2O_3 (Beijing Chemicals Co. Ltd., Beijing, China) in 2 mol/L hydrochloric acid (Tianjin Zhenxing Second Chemical Co. Tianjin, China).

The analyte was freshly prepared from the stock solutions. The concentration of the analyte for arsenic was 50 $\mu\text{g/L}$, containing 5% (V/V) hydrochloric acid, 5 g/L thiourea (Shanghai Chemical Reagent Co., Shanghai, China) and 5 g/L ascorbic acid (Shanghai Chemical Reagent Co., Shanghai, China). The blank sample just contained the same concentrations of hydrochloric acid, thiourea, and ascorbic acid as the analyte, but was arsenic-free.

Potassium tetrahydroborate (KBH_4) (Shanghai Chemical Reagent Co., Shanghai, China) solution (10 g/L) containing 5 g/L sodium hydroxide (Shanghai Chemical Reagent Co., Shanghai, China), was prepared by dissolving potassium tetrahydroborate in sodium hydroxide solution just before use.

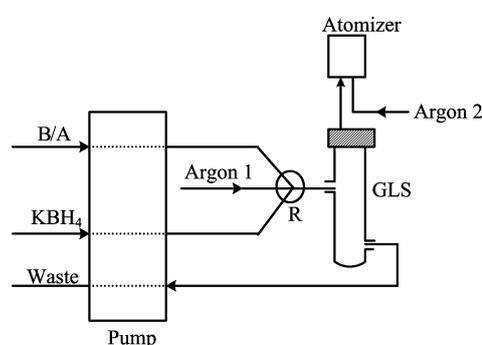


FIG. 2 Schematic diagram of the gaseous atoms generation. A-analyte, B-blank, R-reactor, GLS-gas/liquid separator, Argon 1-carrier gas, and Argon 2-shield gas.

C. Procedure

The computer-programmable operation procedure consisted of four steps. (i) The arsenic samples solution was sucked for 18 s into the reactor. Meanwhile, the concentrated KBH_4 solution was pumped into the reactor. (ii) The sampling volume was 1.2 mL. In step 2, the peristaltic pump paused for 6 s, and the reagents were mixed well in the reactor, where the concentrated KBH_4 was also reacted with the sample solution, producing AsH_3 . (iii) The carrier gas was pumped through the reactor to flush the sample solution into the gas-liquid separator, where the gas of AsH_3 went to a quartz tube atomizer. At the same time, the waste liquid was moved away from the system. This step took 21 s. (iv) 6 s duration was kept to make ready for the next measurement.

III. RESULTS AND DISCUSSION

A. Optimization of experimental conditions

In order to obtain the optimum conditions for the present method, the effect of different experimental parameters, such as carrier flow rate, shield flow rate, and sample acidity was investigated in detail. A solution containing 50 $\mu\text{g/L}$ of As(III) and the spectral line at 234.99 nm were used in the optimization experiment through-out.

1. Argon carrier flow rate

Generally, the flow rate of carrier gas has a serious influence on transport efficiency of generated AsH_3 vapor away from the gas-liquid separator. The effect of argon carrier flow rate in the range of 100-800 mL/min, an allowable maximum was range of flow rate in the present AFS instrument, was studied using the designed program. As is seen in Fig.3, the fluorescence signal increased along with the increase of argon carrier flow rate before a maximum was obtained at the flow rate of 500 mL/min, then the signal decreased rapidly. The rate above this value is so quick that AsH_3 can not be atomized completely, so the argon flow rate of 500 mL/min was chosen.

2. Argon shield flow rate

The Argon shield flow rate is closely relative to the atomization of analytes. The preliminary experiment showed that the flame was too instable when argon shield flow rate was higher than 1600 mL/min. On the other hand, the possible spectra absorption by atoms themselves could occur when argon shield flow rate is too slow. Therefore, the effect of argon shield flow rate

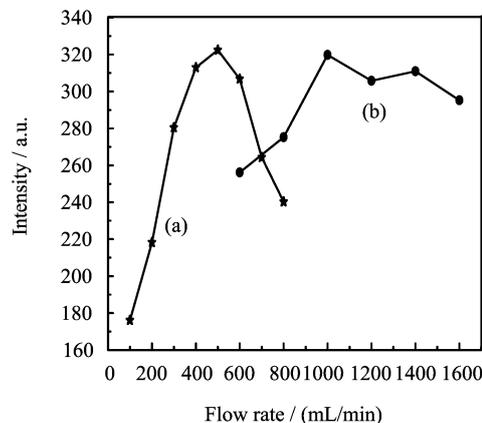


FIG. 3 Effect of argon carrier flow rate on the fluorescence spectrometry of AsH_3 . (a) Carrier gas. (b) Shield gas.

varying from 600 mL/min to 1600 mL/min was investigated in detail. From Fig.3, it can be seen that, slower than 1000 mL/min, with the increase of argon shield flow rate, the signal increased gradually. When the flow rate of argon shield gas got above 1000 mL/min, the signal decreased slightly and became instable. The possible reason was that a high flow rate of argon shield would produce an instable flame and enlarging the flame volume thus diluted the arsenic atoms, and this caused the decrease and instability of the signal. As a result, 1000 mL/min argon shield flow rate was chosen.

3. Analyte acidity

The generation and volatilization rate of AsCl_3 is strongly dependent on the HCl concentration used in the sample solutions. The effect of HCl concentration of the analyte varying between 1% and 8% was studied. No signal was determined when HCl concentration in the reagent is lower than 3%, since the production of AsCl_3 was too small. As expected, As(III) was found to give the best response when concentrated hydrochloric acid (5%) was used as the reagent. Therefore, the concentrated hydrochloric acid was chosen.

4. Pre-reducing reagent

The effects of mixed reducing agent (ascorbic acid+thiourea) concentration on the fluorescence signal responses were studied and the results are given in Fig.4. When the mixed reducing agent concentration was lower than 5 g/L, the fluorescence signal response increased gradually. While the concentration got higher than 5 g/L, the fluorescence signal responses were nearly constant. As a result, 5 g/L ascorbic acid+5 g/L thiourea was used as the optimum reducing reagent in our work.

TABLE I Lines analysis of SR-AFS excitation spectra^a.

	Wavelength/nm		Potentials/eV	Possible transition
	This work	Reference		
I	228.85	228.81 [30]	6.770-1.353	5s(² P _{3/2})→4p ³ (² D _{5/2})
	234.99	234.98 [30]	6.588-1.313	5s(² P _{1/2})→4p ³ (² D _{3/2})
	243.70	243.72 [30]	6.398-1.313	5s(⁴ P _{3/2})→4p ³ (² D _{3/2})
II	195.89	195.891 [31]	8.64-2.312	6s(² P _{3/2})→4p ³ (² P _{3/2})
	204.74	204.757 [31]	8.31-2.255	6s(⁴ P _{1/2})→4p ³ (² P _{1/2})
	214.46	214.408 [31]	8.04-2.255	4d(² P _{3/2} [*])→4p ³ (² P _{1/2})
	237.06	237.077 [31]	7.55-2.312	5s(² D _{5/2})→4p ³ (² P _{3/2})
	222.68	—	7.83-2.255	4d(⁴ P _{3/2} [*])→4p ³ (² P _{1/2})
III	224.40	—	7.84-2.312	4d(⁴ P _{3/2} [*])→4p ³ (² P _{3/2})
	224.80	—	7.80-2.312	4d(⁴ P _{5/2} [*])→4p ³ (² P _{3/2})

^a 4d(²P_{3/2}^{*})=75%4d(²P)+12%4d(⁴F), 4d(⁴P_{5/2}^{*}) [31]=56%4d(⁴P)+31%4p⁴(⁴P), 4d(²P_{3/2}^{*})=54%4d(⁴P)+27%4p⁴(⁴P).

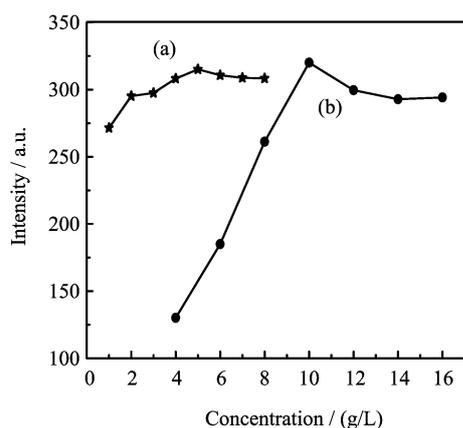


FIG. 4 Effect of flow concentration. (a) KBH₄. (b) Ascorbic acid+thiourea.

5. Concentration of KBH₄ solution

The effect of concentration of KBH₄ solution in the range of 4-16 g/L was studied. As Fig.4 shows, for concentrations above 10 g/L, there was too much hydrogen gas and the concentration of arsenic atoms in the atomizer would be diluted, and the fluorescence signal decreased. Also, the noise of flame was increased, and reproducibility got poor, so a solution of 10 g/L KBH₄ was chosen in this work.

B. SR-AFS excitation spectrum

The atomic fluorescence spectrum of arsenic is very complicated. Subter-190 nm is a vacuum ultraviolet area, which has rigorous requirements for apparatus and surroundings, but with less importance for routine experiments, so 190 nm was selected as initial scanning wavelength. Beyond 250 nm, the flame background is

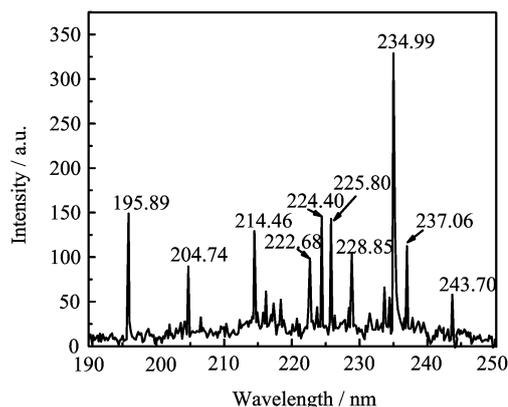


FIG. 5 SR-AFS excitation spectrum.

too high to permit accurate measurements [30]. Considering demands for sample quantity of flow injection and scanning time, 250 nm was taken as the terminal scanning wavelength. The analyte was scanned 5 times with 0.2 nm as scanning interval. The results for a blank sample were regarded as background. Figure 5 shows the SR-AFS excitation spectrum of the analyte.

From Fig.5, arsenic atoms are excited to many different energy levels by synchrotron radiation. The spectral line of the highest intensity appears at 234.99 nm. Considering the sampling interval and signal-to-noise ratio, the ten spectral lines were distinct and well resolved. The lines are basically consistent with those recorded in the literature [30,31]. The central wavelengths have a little excursion because of gaseous atomic pressure augment and atoms collision with each other. There are three spectra lines, which have not been published before.

C. Excitation potentials and transition processes

Excitation potentials and possible transition processes of ten spectral lines are shown in Table I. The lines all have relatively high excitation potentials, moreover the potentials above 6.770 eV excited by existent light sources for atomic fluorescence are seldom recorded. The data of wavelength in section II have never been reported by the means of atomic fluorescence spectrometry, which indicates that synchrotron radiation has better excitation intensity and can offer more energy to atoms for more high-energy transitions. The data labeled with * were calculated to be compositions of even-parity energy level with less than 75% purity using LS representation [31]. The data of wavelength in section III have never been reported, we have repeated the experiments several times and the three spectra lines all appeared at the same wavelength with considerable intensity, so the three lines cannot be attributed to interference atoms. The wavelengths in this section were between 226.69-220.60 nm, in which range there were three spectra lines of arsenic atom listed in the Ref.[31], all the excitation energy levels of the three lines were not pure, but were combinations of different degrees of $4d(^4P)$ and $4p^4(^4P)$. Accordingly, we can conclude that the excitation energy levels of the three lines were also attributed to the combination of different degrees of $4d(^4P)$ and $4p^4(^4P)$, which were excited for the first time by the novel light source, synchrotron radiation. Exact determination of the combination would require further study. The data of spectral lines in section III have not gotten enough attention, maybe due to their high excitation potentials, non-resonance transitions, and narrow wavelength distances between each other.

D. Generation of the prominent line

Researches and applications of the prominent line at 234.99 nm, as shown in Fig.5, will decrease detection limit and enhance sensitivity greatly. The Ref.[30] proposed that the relatively high fluorescence intensity of the 234.99 nm line is an example of thermally-assisted direct-line fluorescence, which is due to the low energy difference between the $5s(^4P_{5/2})$ and the $5s(^2P_{1/2})$ levels (0.031 eV) and the favoured $5s(^2P_{1/2}) \rightarrow 4p^3(^2D_{3/2})$ transition. Moreover, the $5s(^4P_{5/2})$ level can only be populated by absorption of the 189.0 nm ($5s(^4P_{5/2}) \rightarrow 4p^3(^4S_{3/2})$) line, thus it can be proposed that there is a $4p^3(^4S_{3/2}) \rightarrow 5s(^4P_{5/2})$ transition directly radiated by light source and then $5s(^4P_{5/2}) \rightarrow 5s(^2P_{1/2})$ transition by the support of flame energy.

The line at 234.99 nm in this work indicates that atoms on the $4p^3(^2D_{3/2})$ level absorb energy and transfer to the $5s(^2P_{1/2})$ level directly. According to the

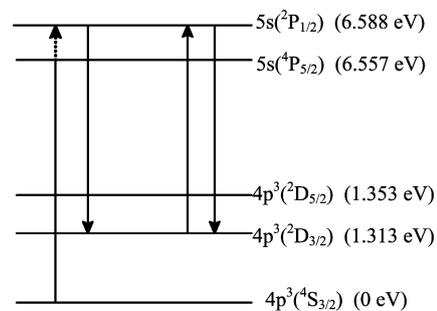


FIG. 6 Model of energy transition processes of arsenic atoms at 234.99 nm.

intensity, it can be concluded that the transition has big probability and generates resonance fluorescence. Because the degeneracy of $5s(^2P_{1/2})$ and $4p^3(^2D_{5/2})$ is mismatch, belonging to transition-forbidden, excited atoms all relax to $4p^3(^2D_{3/2})$ state.

In summary, it is proposed that the fluorescence line at 234.99 nm is probably the co-effect of resonance transition and thermally assistant non-resonance transition. Since the excitation spectrum of arsenic atomic fluorescence was detected in present work, it just stood for the contribution of resonance transition. It can be concluded that use of the line at 234.99 nm for quantitative analysis of arsenic can reduce the limit of detection and enhance the sensitivity greatly.

According to discussions above, the transition model of arsenic atom at 234.99 nm is proposed, as shown in Fig.6.

IV. CONCLUSION

Higher excitation transitions are proposed by using synchrotron radiation to excite atomic fluorescence. Synchrotron radiation has convenient wavelength scanning technology, which can support studies on atomic spectral lines, especially on the mechanism of non-resonance transitions. This study utilizes a novel SRAFS system, and ten excitation spectral lines of arsenic atoms are detected. The excitation potentials and transition processes are discussed. For the prominent line at 234.99 nm in particular, the transition mechanism and the energy level transition model are proposed. This work has accomplished the elementary study on combination of the novel light source, synchrotron radiation the classical testing technique, and atomic fluorescence spectrometry. In following work, we will focus on applying SR-AFS on quantitative analysis of environmental and biologic samples.

V. ACKNOWLEDGMENTS

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