

# Arsenic Determination in Geological Samples by Atomic Fluorescence Spectrometry

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## Abstract

**An atomic fluorescence method was established for the determination of arsenic in geological samples. After sample digestion, arsenic reacts with potassium borohydride in a specific medium to produce volatile hydride. The fluorescence of characteristic wavelength is emitted under the irradiation of argon loaded quartz atomizer light source, and the fluorescence intensity is proportional to the content of elements.**

## Keywords

**Atomic Fluorescence; Geological Samples; Arsenic.**

## 1. Introduction

It is well known that As at trace and ultra-trace level can be determined by AAS, ICP-AES, ICP-MS, ICP-OES and CVG-AFS[1-4]. AFS was the most frequently-used analytical method in China because it had a wide linear range, high sensitivity, low background noise, convenient operation, and low cost. Chemical vapor generation is an efficient method to separate ultra-trace species from sample matrix of Chinese herbs, which can improve the detection limit by utilizing an optimized flow system.

The content of arsenic in regional geochemical river sediment and soil components is generally in the order of  $10^{-6}$  to  $10^{-8}$ , which is a trace analysis category in the field of analytical chemistry. The primary condition for trace analysis methods is that the sensitivity of the selected method should be slightly lower than the level content in the detected object, in order to achieve a high reporting rate. Many predecessors in chemical analysis have utilized the characteristic that arsenic and hydrogen can easily form covalent compounds, and used the addition of borohydride to cause a hydride reaction of arsenic element. This allows trace arsenic in the solution to be vaporized and transferred from the food (including the matrix) in the preparation solution, and directly introduced into the flame by silkworm gas, thereby minimizing matrix interference in the flame; Combined with non dispersive atomic fluorescence detection technology, the background absorption is significantly reduced compared to using dispersive instruments. This method uses AFS-820 atomic fluorescence spectrometer to determine arsenic in geochemical exploration samples. The detection speed is fast, the operation is simple, and the analysis accuracy is high, which meets the requirements of batch testing in the laboratory.

## 2. Experiment

Instrument and Reagents.

Atomic fluorescence spectrophotometer; Arsenic hollow cathode lamp; The carrier gas and shield gas were N-50 purity compressed argon (99.999%) of BOC GAZY (China). 18.2M $\Omega$ .cm de-ionized water from a Mille-Q system (Millipore, Milford, MA, USA). The commercial standard stock solutions were purchased from the National Standard Material Center of China (1.0 g L<sup>-1</sup> of As) and stored in the refrigerator at 4 °C. The As working standard solutions were in 5% (v/v) HCl, diluted by the stock solutions. Potassium tetrahydroborate solution was in 1% (w/w) KOH

solution, and dissolving the solid  $\text{KBH}_4$  of Xi'an Chemicals Co., China. The HCl solution was prepared by GR grade HCl from Xi'an Chemicals Co., China.

### 3. Results and Discussion

1) The selective fluorescence intensity of the lamp current and negative high voltage increases with the increase of the lamp current and negative high voltage of the photomultiplier tube. The increase of negative high voltage is beneficial to the improvement of sensitivity, but the reduction of linear range is considered comprehensively. The lamp current is 60 mA and negative high voltage is 300V.

Observation height was very important to the fluorescence signals of As, which is the distance from the top of the atomizer to the point where the atomic fluorescence signal is generated. For As element, the intensities were decreased slowly. Take signal-to-noise ratio into consideration of this method and signal intensities, the observation height was selected at 8 mm.

2)  $\text{KBH}_4$  was utilized as reductant and hydrogen supply maintaining the argon-hydrogen flame, which can significantly affect the reaction progress and the stability of argon-hydrogen flame. The results of potassium borocyanide dosage show that too low or too high concentration of potassium borocyanide will lead to the decrease of sensitivity, the concentration of potassium borocyanide at 1%~2% is more stable, so the concentration of potassium borocyanide at 1.2% is used as a reducing agent.

3) In this method, hydrochloric acid was selected as the carrier. Since the generation efficiency of chemical vapors extremely depended on the acidity of the reaction solution, the intensity of analyzed elements can be affected by the concentration of HCl. Moreover, the stability of the reaction system is related to the concentration of HCl as well. When the concentration of hydrochloric acid was 1% and 10%, the fluorescence intensity was stable, and 5% hydrochloric acid was used as the medium.

#### 4) Standard Curve

There was a linear relationship between fluorescence intensity and concentration, when As was 2~50.00 $\mu\text{g/L}$ . Linear equation was  $Y=74.65x$ ,  $r=0.9993$ .

#### 5) Precision test

The relative standard deviation (RSD%) of amylase samples was calculated for 7 times, and the relative standard deviation (RSD%) of arsenic was 1.1%.

#### 6) Standard addition and recycling experiment

The arsenic standard solution was added to amylase samples, and the arsenic standard recovery 99.2%, which indicated high method accuracy.

### 4. Conclusion

This method is suitable for the determination of arsenic in geological samples by hydride atomic fluorescence method. The hydride generation atomic fluorescence spectrometry was a highly sensitive, simple and feasible method for determining As. The results are in line with the national standard limit.

#### 4.1. Measurement Results

Sampling and determination were conducted on three sets of devices: hydrocracking, I atmospheric and vacuum distillation, and II atmospheric and vacuum distillation. A certain amount of arsenic standard was added to each sample separately, and the recovery rate was calculated.

## 4.2. Interference Ion Influence

Under selected conditions, it was found that transition elements such as copper, cobalt, nickel, and iron have serious interference with the occurrence of hydrides. In addition, the majority of hydrides can form and there is also serious mutual interference between the elements, which may cause co precipitation or adsorb hydrides and cause them to decompose in contact, slowing down or stopping the occurrence of hydrides. In addition, it may also be due to the consumption of a portion of sodium borohydride by interfering elements, resulting in a decrease in its effective concentration and insufficient reduction of analytical elements. In the face of these interferences, this method overcomes the interference by changing the way hydride occurs by using intermittent flow method. Through experiments, the interference can be ignored.

## 4.3. Precautions During the Analysis Process

① Distilled water: This method must use high-purity distilled water, deionized water, or water with higher purity. The deionized water must be stored in an inert container and should be removed through a silicone tube during use, as some glassware may contain very small amounts of arsenic and other elements.

② Reagents: Due to the trace level of arsenic determined by this instrument, the chemical reagents used in the analysis process are an important cause of manufacturing pollution. For example, hydrochloric acid often contains arsenic, so impurities can be checked before use. In addition, all solutions used should be prepared during analysis, otherwise it will have a significant impact on the results

## References

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