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Economical Alternatives for High Sensitivity in Atomic Spectrometry Laboratory

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Abstract

The most commonly used analytical tools for determination of elements at trace levels are atomic absorption spectrometry (AAS), inductively coupled plasma, optical emission and mass spectrometry (ICP-OES and ICP-MS) and atomic fluorescence spectrometry (AFS). Although sensitive plasma techniques are becoming predominant in most of the western laboratories, AAS keeps its importance in developing countries. Simple and inexpensive ways of enhancing sensitivity will be described for laboratories equipped with only a flame AA spectrometer. Although there are many chemical preconcentration procedures to improve sensitivity of flame AAS, only some *atom trapping* techniques will be included here. One kind of atom trapping device is a slotted quartz tube (SQT) used for *in situ* preconcentration of analyte species followed by a rapid revolatilization cycle to obtain an enhanced signal. These devices provide limits of detection at a level of $\mu\text{g L}^{-1}$. Another kind of atom trapping involves use of vapor generation technique and quartz or tungsten atom trapping surfaces. The analytical steps consist of the generation of volatile species, usually by hydride formation using NaBH_4 , trapping these species at the surface of an atom trap held at an optimized temperature and finally re-volatilizing analyte species by rapid heating of trap. These species are transported using a carrier gas to an externally heated quartz tube as commonly used in hydride generation AAS systems; a transient signal is formed and measured. These traps have limits of detection in the order of ng L^{-1} .

Keywords: *Atomic absorption spectrometry, vapor generation, atom trapping, quartz traps, tungsten traps.*

Introduction

Determination of elements at trace levels continues to be one of the most important issues of analytical chemistry. Accurate and sensitive techniques are needed to solve problems related to low concentration levels of trace elements regarding many controversial issues in fields of environment, health and technology. The most often employed tools in this area are atomic absorption spectrometry (AAS), inductively coupled plasma, optical emission and mass spectrometry (ICP-OES and ICP-MS) and atomic fluorescence spectrometry (AFS) that is used less often than the others.

In addition to accuracy and sensitivity, another

important issue in trace analysis laboratory is the availability of economical methodologies. Economy in trace analysis laboratory is important both regarding the initial cost for purchasing an instrument and for its running costs. For this reason, although sensitive plasma techniques such as ICP-OES and ICP-MS are becoming predominant in most of the western laboratories, AAS keeps its importance in developing countries. AAS instruments are available in most laboratories and running costs are reasonable where Ar and other consumables for plasma spectrometry constitute a significant obstacle for many laboratories with limited budgets. Using electrothermal atomic absorption spectrometry (ETAAS), it is possible to carry out analyses at very low limits of detection; however, in this case the cost of instrumentation is almost doubled

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and graphite atomization tubes are not inexpensive consumables. In general, flame AAS (FAAS) technique can be used at only a level of mg L^{-1} while current analytical problems in environmental, medical and other areas require better capabilities at levels of $\mu\text{g L}^{-1}$ or even lower; these demands can be met in general by ETAAS, ICP-OES or ICP-MS. In this presentation, simple and inexpensive ways of extending sensitivity limits will be described for laboratories equipped with only a flame AA spectrometer, so that analysis at levels of $\mu\text{g L}^{-1}$ or lower will be possible. Two approaches will be discussed and reviewed regarding the problems mentioned above; these are namely, *slotted quartz tube atom trap* for improvement of sensitivity in flame AAS and *quartz and metal atom traps* used with vapor generation methods. Scientific and experimental evolution of these techniques will be described and discussed. In this study, mostly the AAS traps developed in our laboratories will be covered and some other examples from literature will also be mentioned.

Slotted quartz tube atom trap

Since the early days of AAS, researchers have noted that some important characteristics in flame AAS are responsible for the limitation in sensitivity; these were, i. *Dilution of sample* with flame gases, ii. *Low nebulization efficiency* causing only 1-10% of the sample being transported to atomizer and iii. *Low residence time* of analyte atoms (few ms) in flame atomizer. Introduction of graphite furnace atomizer by L'vov eliminated these disadvantages to a large extent; however, many users had the desire of preserving the simplicity of flame atomization. Therefore, alternative solutions were also investigated. These attempts are given in a very informative review article [1]. Among the attempts of improving sensitivity by adhering to flame AAS was *slotted quartz tube* suggested by Watling [2]. This was a *slotted quartz tube (SQT)* with two slots at an angle of 120° with respective each other; the device was positioned on top of a flame atomizer where the laminar flame was allowed to enter the slot below the tube. The dimensions of the tube could be designed to give the largest overlap between the source beam and the analyte atoms to give the best absorbance signal and the lowest noise. Flame atomizer is used in its conventional configuration; the presence of SQT causes an enhancement in sensitivity that is typically 2-5 times for some volatile atoms such as Cd, Zn, Se, In, Pb etc. This improvement, although quite small, was interesting and has been used by many researchers as well as the practicing chemists.

Another interesting device was so called a *water cooled U-tube trap* [3]. This device, a simple silica tube, was also positioned on the flame atomizer; tap water was circulated through the U-tube. When sample solution was aspirated in the usual manner, analyte atoms were condensed and collected on the relatively cold surface of the tube. At the end of the collection cycle, water circulation was ended and water inside the tube was replaced by air; the silica tube was therefore heated up rapidly causing reatomization of the collected analyte species; a transient signal is obtained as the source beam is situated nearby the top of the U-tube.

A third kind of device for atom trapping consists of a water-cooled U-tube placed in a slotted quartz tube combining the advantages of both systems; this is named as *integrated atom trap* [4]. In this study, the slotted quartz tube used in *atom trapping mode* will be described. The use and performance of these traps [5], studies regarding the trapping mechanisms [6] and interferences [7, 8] have been reported previously.

Regarding the SQT atom traps (SQT-AT) presented in this study, the following developments and novel analytical approaches have been introduced [5-8] as compared with the original SQT described by Watling [2].

The device is used not only for momentary enhancement of FAAS signals, but analyte atoms are preconcentrated on SQT inner surface and subsequently revolatilized/reatomized to form the signal. Signal enhancement is in the range of 50-200 depending on the conditions and analyte element. Therefore, as compared with the initial use of SQT that gives an enhancement of 2-5 times, significant improvement in sensitivity enhancement has been achieved.

The preconcentration of analyte atoms will be termed as *collection*. Although the release mechanism is not known exactly, this stage is safely termed as *revolatilization* which may represent the event in both cases where the released species are atoms or molecules. In order to affect revolatilization, a very simple procedure is applied that is called *organic solvent revolatilization*. The main stages of the technique are given below.

- i. Using an optimized flame, sample solution is aspirated while SQT is positioned above the flame. This step usually takes few minutes. Analyte atoms are trapped in the inner surface of SQT.

- ii. A rather low volume, 10-50 μL , of an organic solvent, often MIBK (methylisobutyl ketone) is introduced to flame. This alters the flame composition for a very short period of time. This is sufficient to release analyte species from the quartz surface.
- iii. Revolatilization is followed by rapid atomization in flame and a transient signal is obtained.

In earlier stages of the studies, an alternative technique was used; this was called *flame alteration* that consisted of introducing excess fuel (acetylene) into the flame gas stream to effect revolatilization following analyte collection. Although the both techniques provided comparable sensitivities, it was found that the first technique, *organic solvent revolatilization* is much easier and since no extra gas manifold was needed. MIBK is simply introduced into the flame by suction as any sample solution is treated.

Some of the analytical figures of merit for SQT-AT system are given in Table 1. The detection limits reported come close to the performance of ETAAS. Enhancement values were found by the ratio of characteristic concentration for flame operation to that by SQT-AT. The peak height values were used for the signals. The most important figure of merit here is E, enhancement; because, limit of detection and sensitivity is largely dependent on the age of the instrument and the conditions of the source lamp as these parameters directly affect signal to noise ratio.

Table 1. Limits of detection for SQT-AT; 2.0 minutes of collection period and organic solvent revolatilization were used [5,8].

| Analyte | LOD (3s), ng mL ⁻¹ | E (Enhancement) |
|-----------------|-------------------------------|-----------------|
| Cd ^a | 0.4 | 137 |
| Cu ^b | 3.7 | 51 |
| Pb ^a | 3.7 | 90 |
| Zn ^b | 0.8 | 73 |

^aFrom the reference 5.

^bFrom the reference 8.

The following experimental parameters were found to be critical in SQT-AT technique. These must be carefully optimized.

- i. Flame composition. Usually a lean or stoichiometric flame is used.
- ii. Distance between the flame head and SQT.
- iii. Suction rate. It has been found that lower suction rate gives better sensitivity for a defined volume of

sample; nebulization efficiency is improved at lower suction rates and so are the trapping efficiency and sensitivity.

Quartz and metal atom traps

Following the observations that analyte atoms can be successfully trapped on the inner surface of SQT, it was then suggested that similar trapping can be realized using vapor generation methods and either quartz or metal traps. In some preliminary experiments, slots were opened on a T-tube commonly used in HGAAS, analyte in hydride form was introduced through the inlet arm of the system, some trapping and subsequent revolatilization was observed for antimony. The next design did consist of a usual HGAAS set-up; some quartz particles obtained by crushing were placed in the inlet arm, near its connection point to the horizontal arm. The location where the quartz particles are positioned served as the trap. This location was heated externally using a resistively heated wire. In a frontier study [9] trapping and signal formation consisted of the following stages:

- i. Lead hydride (PbH_4) was formed by reaction of analyte with sodium tetrahydroborate (III) in a continuous flow (CF) system.
- ii. Analyte vapor separated from liquid stream is directed to quartz T-tube and passes through the trap held at the optimized *collection temperature*; some of the analyte hydride molecules are trapped here.
- iii. At the end of *collection stage*, analyte flow is stopped; the carrier gas stream is altered to assume the optimized composition to assure the best *revolatilization*.
- iv. The trap is rapidly heated to *revolatilization temperature*, release of analyte species takes place and these volatile species are transported to T-tube quartz atomizer.
- v. Signal is formed and recorded as a result of analyte atomization in the measurement zone.

It has been found that the most critical analytical parameters are the temperature of trap for collection and revolatilization, position of trap and composition of carrier gas at both stages of collection and revolatilization. Other parameters such as acidity, concentration of reductant, sample and gas flow rates, length of reaction and stripping coils, design of gas-liquid separator and quartz T-tube atomizer are common to both ordinary HGAAS and Trap-HGAAS systems. After the determination of Pb, on line trapping on quartz surface has been used for determination of Sb both by

chemical [10, 11] and electrochemical hydride generation [12]; the technique has also been applied for determination of Bi [13], As and Se [14]. Cold vapor generation (CVAAS) with a quartz trap has been used for determination of Cd where the quartz atom cell was not heated [15].

Another alternative technique for on-line trapping and HGAAS involves a W-coil as the trap. W-coil atom trap can be resistively heated by passing electricity directly through this device while external heating is required for the quartz trap; therefore, higher heating rates can be achieved for the former. Tungsten coil is taken from a commercial visible tungsten lamp; it can be readily and economically obtained, used and replaced when a new one is needed. The use of a W-coil from a commercial lamp is dated back to 1972 [16]; after the first application there has been a wide interest in use of W-coil as an atomizer [17,18] mostly as an alternative to graphite furnace. W-coil has been used as a trap for determination of Bi [19] and Se [20] by two independent groups at about the same time. W-coil atom trap has the principals similar to quartz atom trap. The tungsten trap is located in the inlet arm of a conventional T-tube quartz atomizer. The trap temperature is conveniently adjusted to optimized values for collection and volatilization stages. W-coil atom trap has also been used for determination of Cd in CVAAS mode [21].

Alternative trap materials have also been suggested for on-line trapping and vapor generation systems; molybdenum strip for determination of As and Se [22] and antimony and bismuth [23], resistively heated platinum for Cd [24] and externally heated Au wire for Se [25] can be mentioned among these studies. On-line vapor generation traps by using quartz or W-coil has detection limits in the order of ng L^{-1} ; some of the examples are shown in Table 2.

Table 2. Examples from performances for quartz and W-coil atom trapping used with vapor generation techniques

| Analyte | Trap | Vapor generation technique | LOD(3s), ng L^{-1} | Reference |
|---------|--------|----------------------------|-----------------------------|-----------|
| Pb | Quartz | HGAAS | 19 | 9 |
| Sb | Quartz | HGAAS | 3.9 | 10 |
| Cd | Quartz | CVAAS | 1.8 | 15 |
| Bi | W-coil | HGAAS | 2.7 | 19 |
| Cd | W-coil | CVAAS | 4.0 | 21 |

Conclusion

Atom trapping, either by using SQT-AT or quartz/metal traps with vapor generation systems, is an economical, simple and sensitive alternative in atomic spectrometry. Most of these devices have so far been used in conjunction with AAS in order to provide economical alternatives; quartz/metal traps can also be used with ICPOES and ICPMS. Detection limits at the level of $\mu\text{g L}^{-1}$ and ng L^{-1} have been obtained for SQT-AT and on-line quartz or W-coil atom traps, respectively. All of these trapping systems can be easily and conveniently constructed in any laboratory; in addition to a simple FAAS instrument, only a peristaltic pump and simple glass and quartz components are required; W-coil can also be inexpensively purchased in the form of a commercial light bulb. These devices enable analytical chemist in laboratories with limited budgets to obtain a level of sensitivity as good as or near to more expensive instruments such as ETAAS and ICPMS.

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