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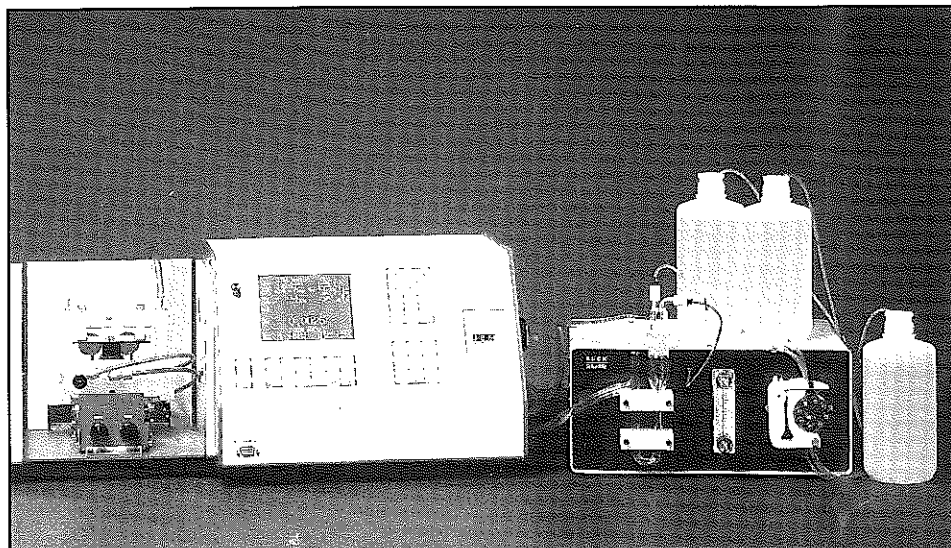
**Optimized analytical conditions for sub-ppb arsenic
and selenium determinations by FAAS**

Buck Scientific Continuous Flow Hydride/Cold Vapor System

For parts-per-trillion level detectability

Overview

The Model-420 is an easily adaptable accessory for Flame AA Spectrophotometers that allows PPT detectability for As, Se, Sb, Sn, Te, Bi and Ge using standard hydride generation procedures. Using inert polymer components and a reliable pumping system, users can quickly switch between flame and hydride.



Features

- Allows superior detection limits for hydride metals compared to graphite furnace AAS, typically in the 100-500 parts-per-trillion range.
- Can install easily and rapidly to existing flame set-up and run within 2 minutes.
- Does not require hydrogen gas
- Continuous flow pump design allows for simple interfacing of intelligent auto-sampler for high-throughput, unattended operation.
- 4 order of magnitude dynamic range using the Buck Model 210VGP AA system for the highest accuracy over a wide range of sample concentrations.....minimizing dilutions and errors.
- Inert tubing gives rapid equilibration time allowing typical throughputs of 50 samples per hour with reproducibilities of better than 2% at the 500 ppt level.
- Optimized procedures for *all* the hydride elements eliminates development time and simplifies operations for the chemist or lab technician.
- Low format footprint requires minimal bench space and unit can be put on a cart or side table.

BUCK
Scientific

*Affordable
Quality*

Optimized analytical conditions for sub-ppb arsenic and selenium determinations by FAAS

ATOMIC ANALYSIS is one of the most popular and wide-ranging instrumental techniques employed in the laboratory today. Atomic absorption instruments, as well as plasma emission spectrometers, can be found in virtually all commercial, industrial, and private laboratories. The applications for the determination of metals are equally numerous, ranging from major (percentage) components in metallurgical materials to minor (ppm) constituents in nutritional analysis and trace (ppb) contaminants in pollution studies. Interestingly, the most environmentally hazardous metals are also the ones that have the least sensitivity by flame atomic absorption spectroscopy (FAAS). Normally, a simple air/acetylene flame is used to vaporize the sample aerosol coming off the nebulizer and create the excitation signal that is measured by the AAS. Elements such as arsenic, selenium, and lead have typical method detection limits in the 0.1-ppm (100-ppb) range, which is significantly higher than most U.S. EPA and state regulatory limits.

A brief history

During the development of classical chemical analytical techniques, it was discovered that certain elements at one

end of the periodic table had the property of being convertible to a somewhat stable, gaseous hydride when reacted with a strong reducing agent, which could then be thermally reduced to the free metal. This is the foundation of the classic Marsh test for arsenic. Protocols for the hydride generation procedure were originally developed using highly reactive metals in the presence of strong acid solution (e.g., zinc in 25% hydrochloric acid or magnesium in 10% sulfuric acid). The gaseous discharge from the reaction flask was purged with inert argon gas and burned either in an air/acetylene flame or, preferably, in an argon/hydrogen flame of an atomic absorption system. This served to 1) thermally decompose the hydride compound into the element and 2) minimize the atmospheric oxygen background absorption, which can obscure hollow-cathode lamp discharges below the 200-nm limit of most system configurations and reduce the signal/noise ratio. As chemical technology advanced and more reagents became available to the analytical laboratory, the strong (and safe) reducing agents sodium borohydride and cyanoborohydride became the reagents of choice in improving both the reproducibility and the overall sensitivity of hydride generation. Other more efficient compounds such as lithium aluminum hydride were too dangerous for routine use in an analytical laboratory. Some researchers also noticed that the presence of certain materials either enhanced or inhibited the formation of the desired hydride

species; these can now be promoted or eliminated, respectively, using specific reagents in the reaction process.

Mechanisms and interferences

There are a multitude of reaction mechanisms involved in the hydride generation process, but basically, the primary reaction of the tetrahydroborate (BH_4^-) anion with acid(s) (H^+) in the presence of certain elements (As, Se) will generate free hydrogen (H_2), covalent metal hydrides (AsH_3 , SeH_4), and boric acid ($B(OH)_3$). The metal hydride of elements such as arsenic, selenium, antimony, lead, tin, bismuth, tellurium, and germanium can then be purged from the reaction vessel and directed to a holding vessel for batch mode analyses or directly to the atomization source for continuous mode testing. The concentration of the borohydride and acid reagents is different for both techniques and for different elements. Copper, nickel, and silver can inhibit the reproducible and quantitative formation of AsH_3 and SeH_4 in solution, but studies have shown that adding potassium thiocyanate or ferric chloride will eliminate these interferences and actually enhance the signal for selenium.

Once the hydride gas sample has been generated, it must be decomposed to produce the atomic vapor that will absorb the resonance energy from the hollow-cathode lamp beam to provide the analytical signal. This is usually done thermally by burning the analyte hydride along with the evolved hydro-

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gen from the reaction, using either a flame or a heated quartz tube. While the flame method was used initially because of its simplicity, it tended to suffer from instability and noise due to the turbulence of the gases involved and the short residence time of the atomic vapor in the dynamic flame environment. Nevertheless, analysts were able to achieve significant improvements in detectability using this procedure. Later, the development of the quartz T-tube revolutionized the applicability of routine hydride generation by providing a more controlled environment for the decomposition of the hydride species and by allowing the atomic vapor to remain in the HCL beam much longer. This increased residence time, much like that of graphite furnace atomic absorption spectroscopy (GFAAS), improved the sensitivity and precision of the technique radically. The outlet from the reaction flask is purged into the quartz T-tube mounted directly over a standard air/acetylene burner head; thus, no special gases or modifications are required, and the change from the direct nebulization to hydride is rapid and simple.

Modes of operation

Original methodologies were developed for discrete sample aliquots by recording the transient signal for the evolved hydride from a reaction vessel containing a relatively large volume (as much as 250 mL) of sample solution. In the batch mode, this concentration ratio gave very good sensitivity but had fairly low throughput and required either a strip-chart recorder to measure the peak height or, more properly, an integrator to calculate the peak area for more accurate and precise data. To accommodate the stringent requirements of the ever-growing environmental industry and industrial hygiene laboratories, efforts were made to develop a continuous flow hydride generation system that would allow rapid, on-line measurements of the hydride metals in solution. Initial attempts gave researchers encourage-

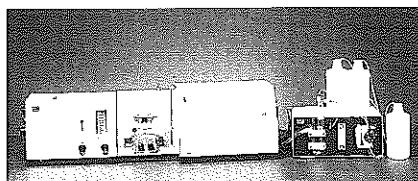


Figure 1 The model 420 continuous flow hydride/cold vapor accessory attached to the 210VGP AA spectrophotometer.

ment because reproducibility was maintained. However, the reaction itself was performed on the fly in a reaction tube rather than contained in a closed vessel; accordingly, overall sensitivity suffered. With refinements in the chemistry and operational conditions being made to optimize the performance of the continuous flow hydride method, some configurations available today can actually exceed the batch hydride systems for speed and data quality.

The following study details the specific requirements for the optimum analysis of arsenic and selenium, the two primary hydride metals of importance for continuous determination using FAAS with a T-tube. The analyses employed the model 210 AA unit (Buck Scientific, East Norwalk, CT)

with UV-enhanced optical components and in-line deuterium background corrector, the model 220 automated graphite furnace attachment (Buck Scientific), and the model 420 continuous flow hydride/cold vapor accessory (Buck Scientific) (see *Figure 1*). After the optimization procedure is defined, comparisons between GFAAS and hydride generation will be shown.

Optimization

Based on the literature references, there are a number of parameters that affect the formation of gaseous hydrides. This article focuses on the following:

- concentration of sodium borohydride
- concentration of acid media
- mixing rate of the reagents and sample (based on liquid flow)
- composition of sparging gas
- rate of sparging gas (based on gas flow)
- interfering metals and chemical correction
- valence state of the analyte (As +3/+5 and Se +4/+6)

The first two items are the most crit-

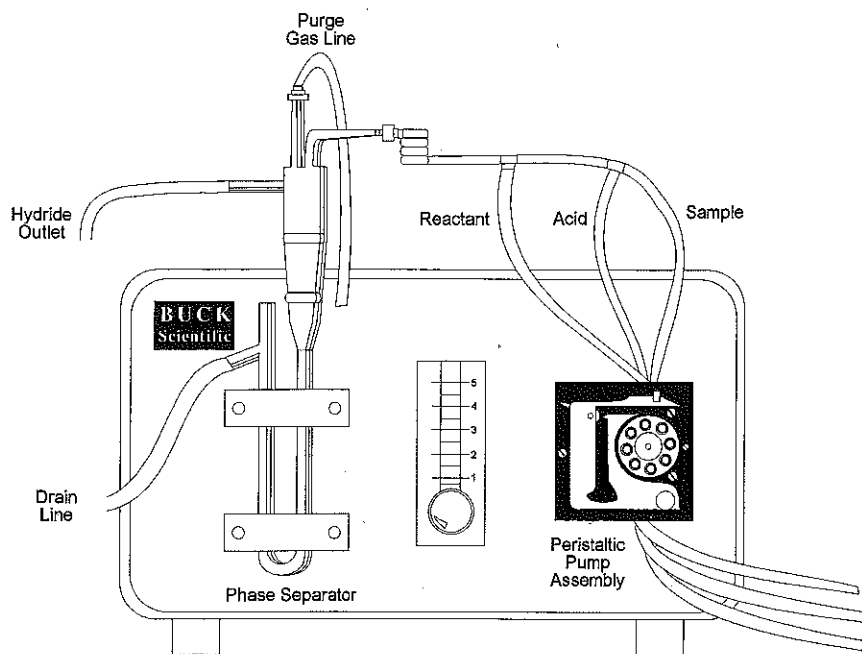


Figure 2 Schematic of the model 420 continuous hydride unit.

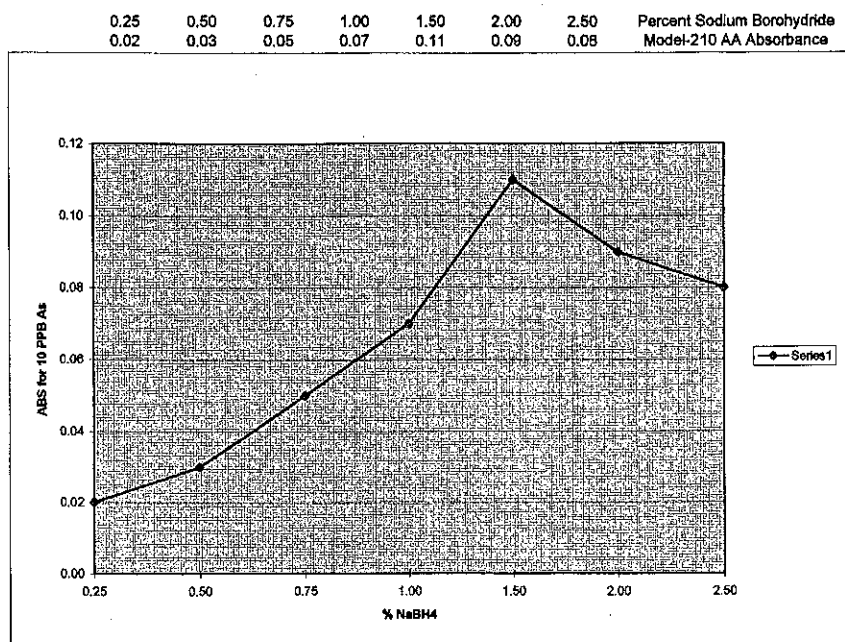


Figure 3 Arsine generation versus reductant concentration.

ical and specific for the elements themselves, while the other variables can be optimized for the specific pieces of instrumentation. The basic gas and liquid flows were tested using a strong 50-ppm arsenic standard, a 2% NaBH₄ solution, and a 20% hydrochloric acid medium as the initial conditions. Settings were optimized based on a maximum signal and a reproducible signal for these solutions. Afterwards, the chemistry itself was fine-tuned for best quality.

Instrumentation

Initially, the instrumentation parameters were set based on the flow characteristics of the hydride unit, the T-tube dimensions, and the AA unit. The three-channel peristaltic pump on the model 420 (Figure 2) is used to deliver sample solution and acid media together first, then mix downstream with the borohydride to produce the hydride. This mixture passes through a reaction coil and then into a phase separator containing a sparging tube. The best reproducibility was seen using a liquid flow of ~8.5 mL/min using inert Acid-Flex PVC pump tubing, for a to-

tal flow of ~25 mL/min. The sparging gas was critical to the rate of decomposition and residence time of the atomic vapor in the T-tube and was optimized at ~1 scfh. Preliminary studies were performed with pure argon as the

sparging gas, but the response of the system was lower than expected. Further investigation revealed that the presence of 1–2% oxygen (or 5–10% air) would enhance the thermal decomposition of the AsH₃ or SeH₄ in the vapor phase rather than on the walls of the quartz T-tube, and gas lines were modified to allow the inclusion of air into the flow. The T-tube itself was placed on a standard mount ~8 mm over the standard burner head of the model 210 AA and heated using a lean flame for optimum temperature. The authors' experience has shown that using 100 ppm ferric chloride (FeCl₃) eliminates the interferences from the higher levels of copper and nickel, because this evaluation standardizes on ferric acid being added to the sample and standard solutions. To eliminate the errors seen from having the metals present in two different oxidation states, the addition of ascorbic acid or hydroxylamine hydrochloride at 0.1% to the sample solution or at 0.5% in the acid solution has proven effective. Use of the more typical potassium iodide

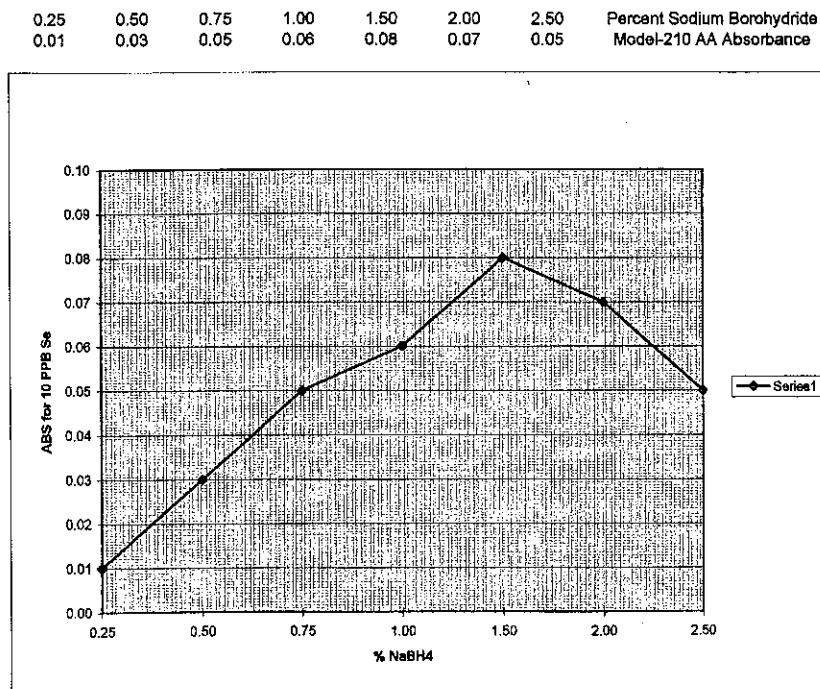


Figure 4 Seline generation versus reductant concentration.

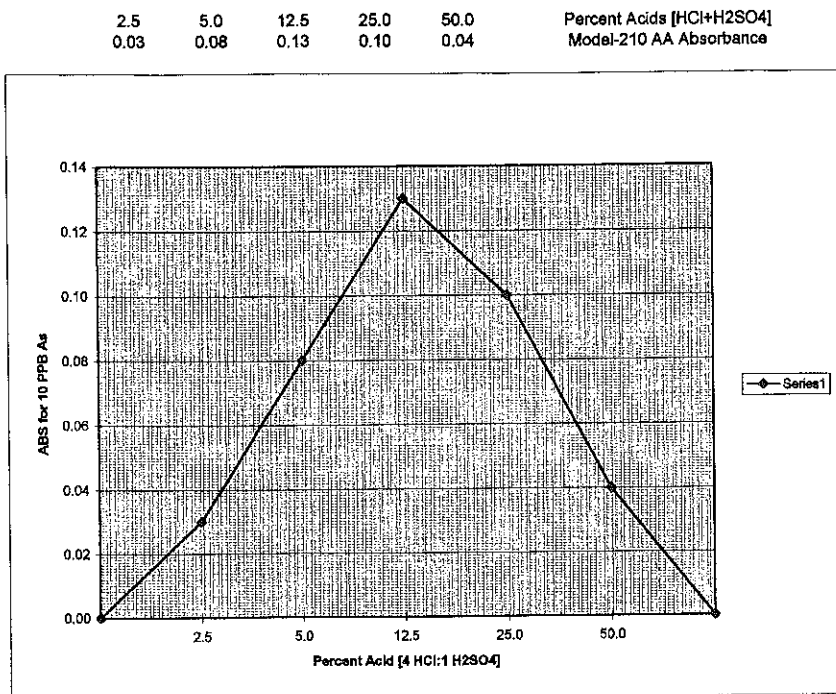


Figure 5 Arsenic generation versus acid concentration.

was avoided because of the number of side reactions that occur and the general lack of control over the secondary reducing abilities using this reagent.

Chemistry

Most references cite sodium borohydride (NaBH_4) concentrations from

0.5% to 5% in a solution of sodium hydroxide (NaOH) from 0.5% to 5%. Since many of these procedures were quoted for batch mode operations, the authors realized that differences in chemical reactivity existed between the batch and continuous modes. A 0.5% NaOH solution was used as a standard to stabilize the varying levels of NaBH_4 being evaluated. At higher concentrations of NaOH , there would be too many competing reactions with the acid and possible thermal effects from the heat of neutralization. Prepared solutions of 0.25%, 0.5%, 0.75%, 1.0%, 1.5%, 2.0%, and 2.5% NaBH_4 were used for this phase of the study. Literature citations of acid concentration were much more diverse, with values in references ranging from 1% hydrochloric acid to 50% mixed hydrochloric/sulfuric acids. The authors' observations showed that hydrochloric acid at the 15% level is about the most frequently used solution for quantitative reduction of hydrides, and the solubility of these gaseous hydrides in acid solution is decreased in the presence of 5% sulfuric acid. This was the initial acid medium used for evaluating the response from the NaBH_4 solutions listed above. The relative response for 10-ppb arsenic is shown in Figure 3, and the relative response for selenium is shown in Figure 4 for the range of NaBH_4 reductant referenced above. It can be seen that both arsenic and selenium response levels off just below 1.5%. This optimizes the formation of hydride with the least formation of excess hydrogen, which contributes to turbulence and some imprecision in the sparging of the gases into the T-tube and also has a tendency to create a flame coming out of the open ends of the T-tube.

Utilizing a mixed acid medium is more popular than using a single acid, based on both experience and literature; a 4:1 ratio of hydrochloric acid to sulfuric acid has been very efficient in previous batch work. It was decided to keep this ratio and to vary the total acid content for the reduction medium. So-

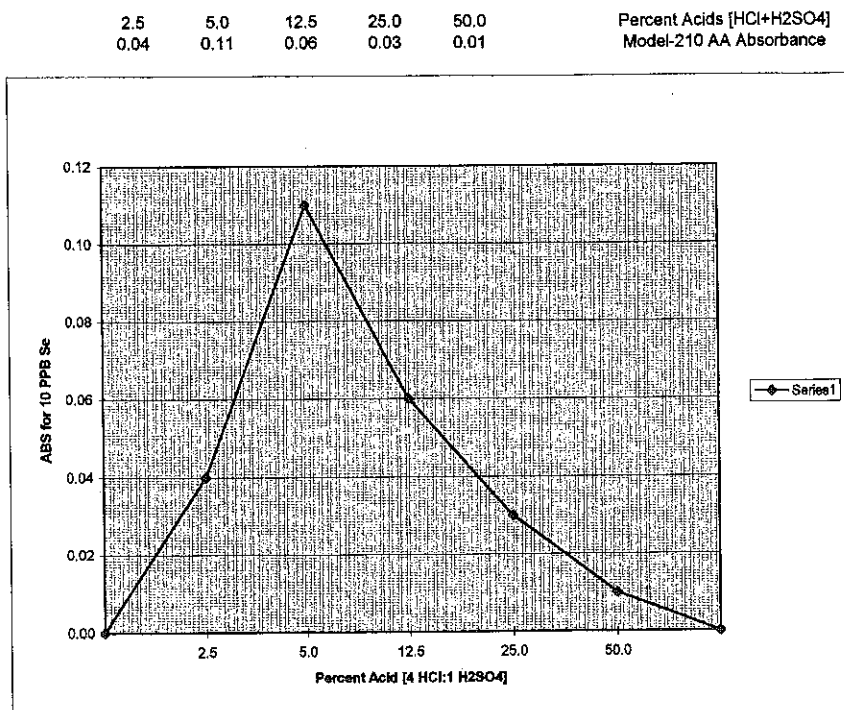


Figure 6 Selenic generation versus acid concentration.

0.50	50.0	1.0	5.0	10.0	25.0
0.006	0.53	0.01	0.08	0.12	0.28

PPB Arsenic
Model-210 AA Absorbance

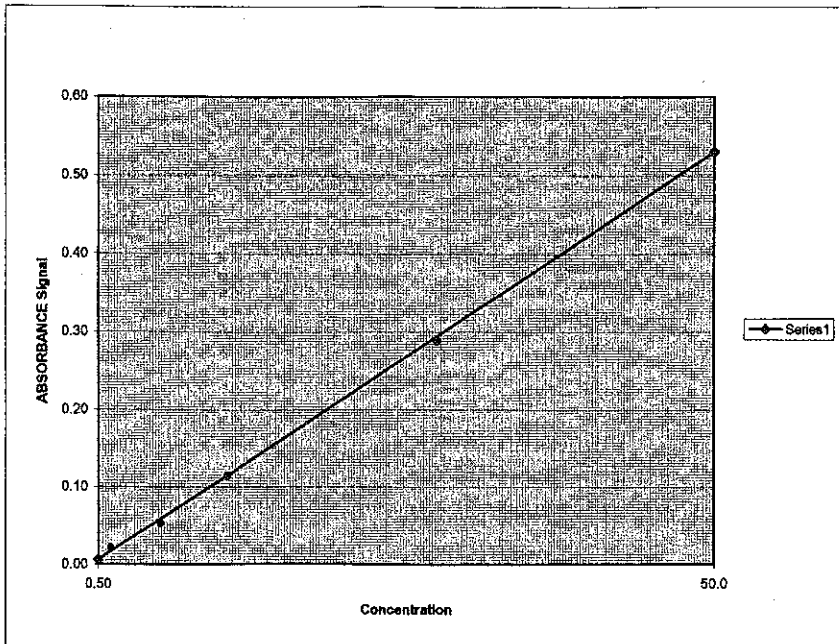


Figure 7 Calibration curve for arsenic by 420-hydride.

0.50	50.0	1.0	5.0	10.0	25.0
0.005	0.42	0.01	0.05	0.10	0.23

PPB Selenium
Model-210 AA Absorbance

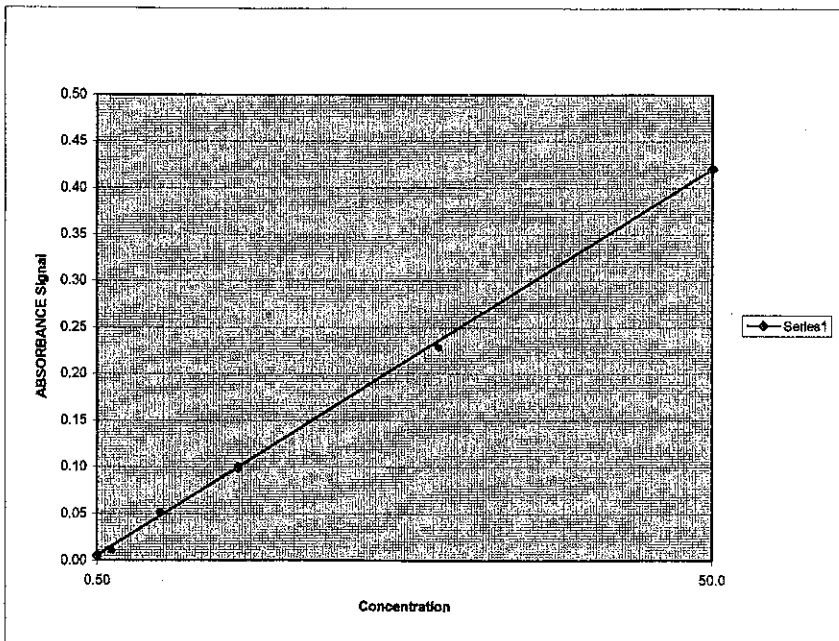


Figure 8 Calibration curve for selenium by 420-hydride.

lutions were prepared containing 2% HCl-0.5% H₂SO₄, 4% HCl-1% H₂SO₄, 10% HCl-2.5% H₂SO₄, 20% HCl-5% H₂SO₄, and 40% HCl-10% H₂SO₄, in deionized water using 37% ACS reagent-grade HCl and 98% ACS

reagent-grade H₂SO₄. (Note: Caution should be used when mixing these acids to prevent splattering and excess fuming.) Dilute the HCl with cold deionized water first; then add the H₂SO₄ slowly while mixing well. Hydroxyl-

amine hydrochloride (0.5%) was added to each solution as a secondary reducing agent as mentioned above. A series of runs was made using these solutions with the optimum 1.5% NaBH₄ in 0.5% NaOH reductant solution as previously determined. The results of the acid media content in the determination of arsenic are shown in Figure 5, and those for selenium are shown in Figure 6. Unlike the NaBH₄ effects, the response of these two elements varied widely with acid content. It can be seen that arsenic is best analyzed in a 1-2.5% acid mix, while selenium is optimized with the 4-1% levels of acids.

Observations

Employing some simple factor analysis, the best conditions for the continuous flow hydride generation analysis of arsenic and selenium can be specified using the above data. With the optimized chemistries, a calibration series from 0.5 ppb to 50 ppb and a blank run were made for arsenic and selenium see Figures 7 and 8, respectively). The performance of the system is detailed below.

Arsenic: 193.7-nm absorption line, 0.7-nm slits, heated T-tube, 1.5% NaBH₄-0.5% NaOH, 10% HCl-2.5% H₂SO₄, 1 scfh argon + 1% oxygen (via air), 6-sec AA integration time, D2 background correction. Calculated detection limit (3-sigma) = 0.15 ppb, typical precision (%RSD) at 1-ppb level = 1.3%, and typical GFAAS detection limit = 0.5 ppb.

Selenium: 194.0-nm absorption line, 0.7-nm slits, heated T-tube, 1.5% NaBH₄-0.5% NaOH, 4% HCl-1% H₂SO₄, 1 scfh argon + 1% oxygen (via air), 6-sec AA integration time, D2 background correction. Calculated detection limit (3-sigma) = 0.35 ppb, typical precision (%RSD) at 1-ppb level = 2.6%, and typical GFAAS detection limit = 1 ppb.

Obviously, the refinements in both the hardware and chemistry seen here can produce very good results exceeding those of GFAA for these hydride elements using the system described. Since these two elements, particularly

arsenic, are of significant concern from an environmental standpoint, the ability to quickly, easily, and accurately analyze them at low levels is a major advantage over the slower graphite furnace technique. As seen, the sensitivities and precisions are very high. The

UV-enhanced optical features of the model 210 AA with the in-line deuterium lamp for background correction present a much better signal/noise ratio than other systems evaluated for this type of work, and the simple model 420 continuous hydride unit presents a

compact and efficient system for routine and high-quality hydride generation. Large-volume, purged carboys can be used for storage of the NaBH_4 and acid solutions, and the sample inlet line can be connected to an autosampler for automatic, unattended operation.