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Manning et al.

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[54] **METHOD AND APPARATUS FOR GENERATING GASES FOR ATOMIC ABSORPTION SPECTROPHOTOMETERS**

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[73] Assignee: **The Perkin-Elmer Corporation**, Norwalk, Conn.

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[52] **U.S. Cl.** ..... **23/230 R**, 23/253 R, 23/259, 356/36, 356/87

[51] **Int. Cl.** **G01j 3/30**, G01n 1/00, G01n 21/58

[58] **Field of Search** ..... 23/230 R, 253 R, 232 R, 23/259, 292, 282; 356/87

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[57] **ABSTRACT**

A gas generation accessory for an atomic absorption spectrophotometer includes a reaction vessel for holding a sample and an acid. The sample includes an element from a group including arsenic and selenium. A dosing column is coupled to the reaction vessel and a gas-tight stopcock is mounted in the dosing column and includes a cavity for holding a metal such as zinc. The stopcock is rotatable for projecting the metal into the acid to cause a reaction to release hydrogen gas. The hydrogen gas in turn reacts with the element in the sample to produce a gaseous hydride. The gaseous hydride is collected in an elastic reservoir and stored under pressure until the completion of the reaction. Thereupon the gaseous hydride in the elastic reservoir is carried into the atomic absorption spectrophotometer and the element appears in a substantial concentration for a relatively short time. This permits the resonance lines of the element to be recorded and the element detected.

5 Claims, 6 Drawing Figures

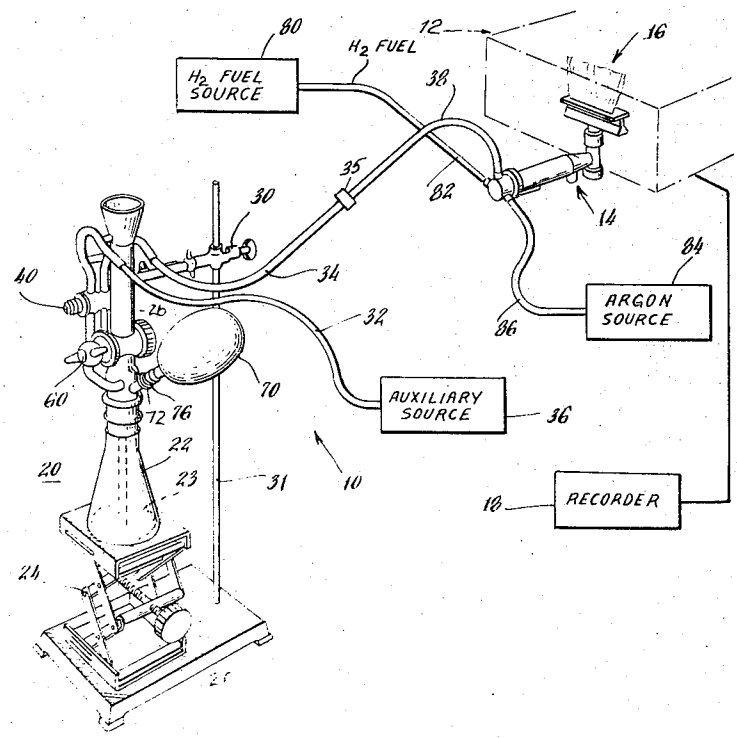
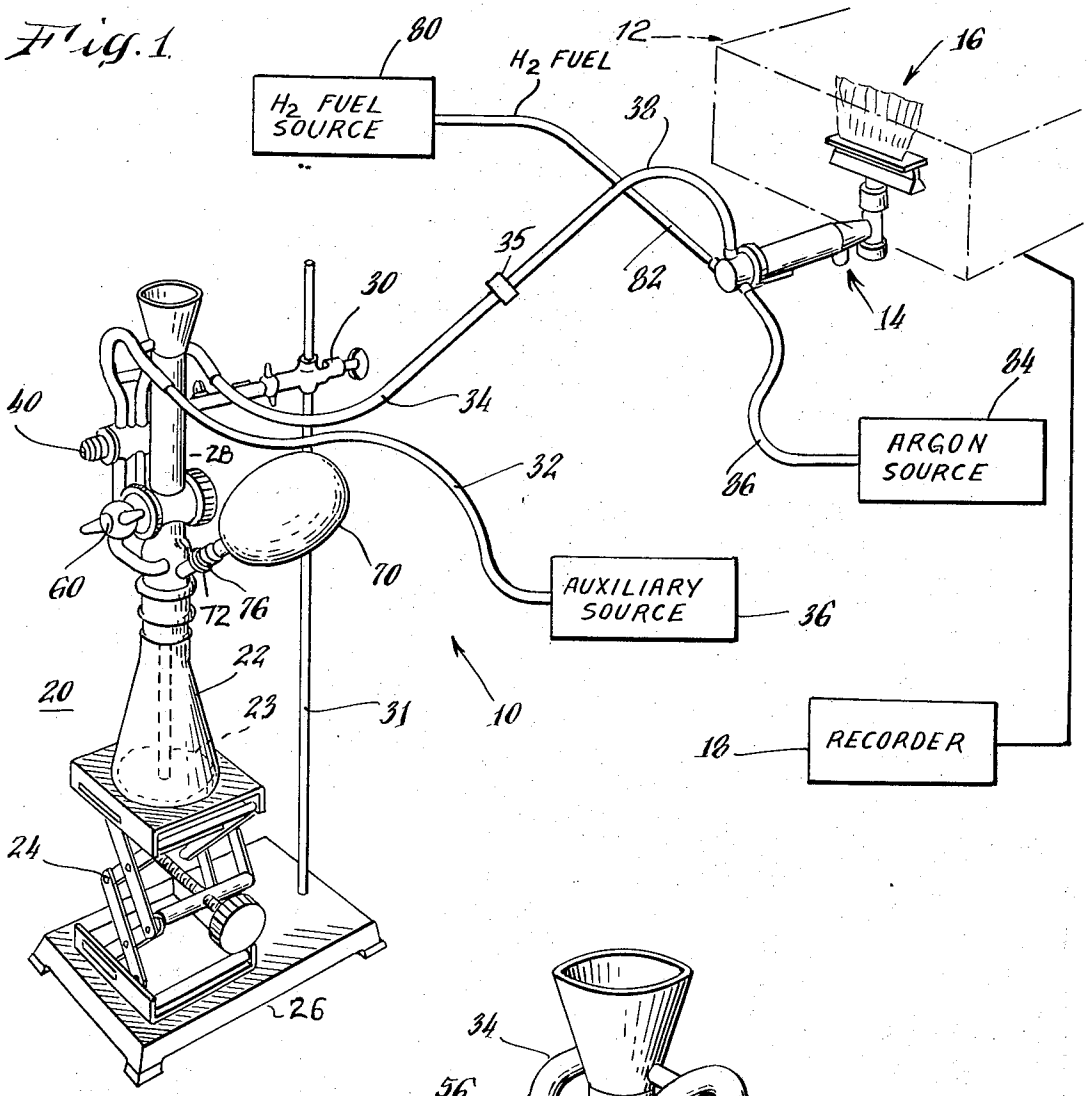


Fig. 1.


80
H_2 FUEL SOURCE
H_2 FUEL
12
16
38
35
82
30
14
84
40
34
ARGON SOURCE
28
32
36
60
70
72
76
AUXILIARY SOURCE
36
22
20
23
31
10
18
RECORDER
24
26

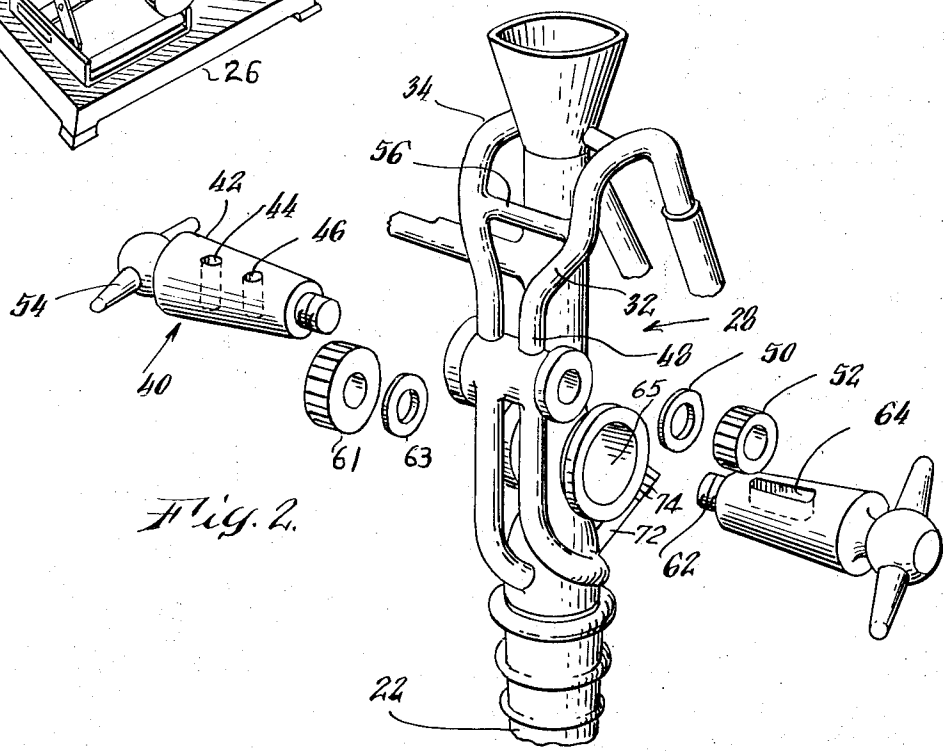

34
56
42
44
46
54
32
28
48
50
52
65
64
40
61
63
74
72
62
22

Fig. 2.

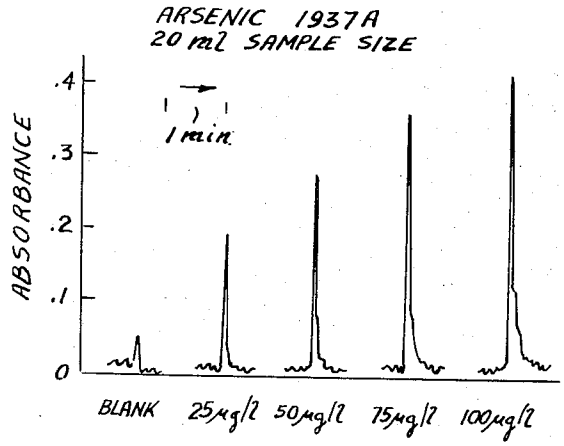


Fig. 3.

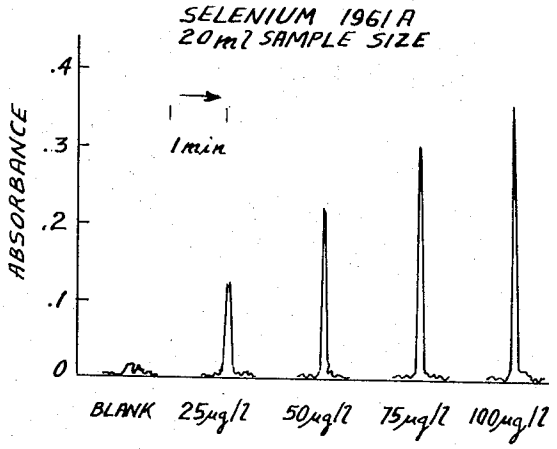


Fig. 4.

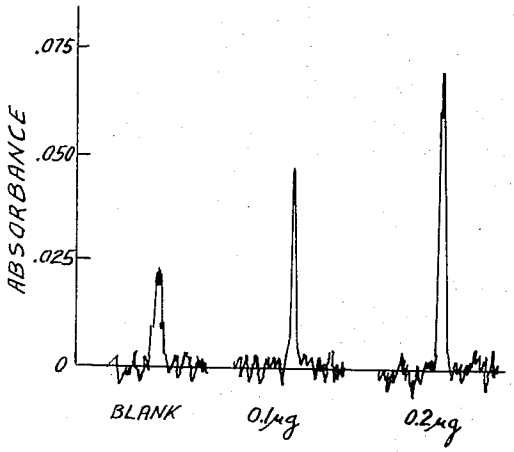


Fig. 5.

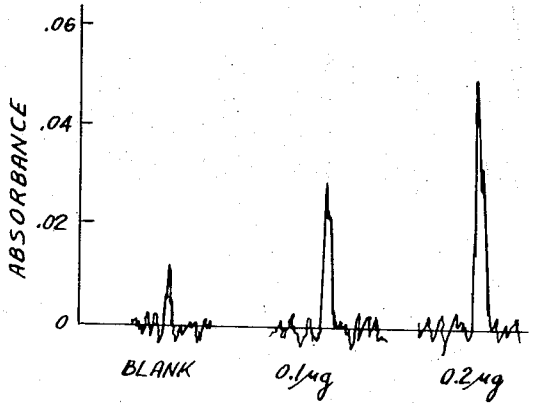


Fig. 6.

METHOD AND APPARATUS FOR GENERATING GASES FOR ATOMIC ABSORPTION SPECTROPHOTOMETERS

BACKGROUND OF THE INVENTION

Certain elements, such as arsenic, present severe problems when the detection of such elements is attempted by standard atomic absorption sampling techniques. This is particularly true when samples contain the element in only very limited trace amounts. In conventional atomic absorption spectrophotometry a solution of the sample is nebulized to provide a vapor and the vapor is atomized in the flame of the spectrophotometer. Presently available nebulizers are only about 5 percent efficient in forming droplets suitable for atomization by the atomic absorption flame. Furthermore the usual rate of aspirating a solution of 3 to 5 milliliters per minute for a length of time on the order of 10 seconds causes the concentration to be extended over this length of aspiration. Consequently when an element such as arsenic appears in minute traces in the sample, the element tends to be indiscernible in the flame. Therefore there is at present a need for providing a technique for detecting elements such as arsenic in trace amounts in a sample.

SUMMARY OF THE INVENTION

A gas generation accessory for an atomic absorption spectrophotometer includes a reaction vessel for holding an acid and a sample containing an element from a group consisting of arsenic and selenium. A dosing column is coupled to the reaction vessel to introduce a metal to release hydrogen gas from the acid to react with the element in the sample to form a gaseous hydride. An elastic gas reservoir is coupled to collect and to store under pressure the gaseous hydride as it is formed. At the completion of the reaction, the expansible reservoir releases the gaseous hydride to provide a surge of the element into the flame of the atomic absorption spectrophotometer to provide a substantial concentration of the element in a relatively short period of time.

DESCRIPTION OF THE DRAWINGS

FIG. 1 is a partially schematic and a partially isometric view of a gas generation accessory for an atomic absorption spectrophotometer;

FIG. 2 is a partially exploded isometric view of the accessory shown in FIG. 1;

FIGS. 3 and 4 are absorbance measurements of selected amounts of arsenic and selenium as measured by the apparatus of FIG. 1; and

FIGS. 5 and 6 are absorbance measurements of arsenic and selenium respectively to determine the minimum traces that are detectable in the apparatus of FIG. 1.

DETAILED DESCRIPTION

In FIG. 1 there is shown apparatus **10** for generating gases for analyzing by an atomic absorption spectrophotometer **12**. The atomic absorption spectrophotometer **12** may for example comprise a Model 403 Atomic Absorption Spectrophotometer manufactured by The Perkin-Elmer Corporation of Norwalk, Connecticut. The spectrophotometer **12** is shown only in outline form in FIG. 1. The spectrophotometer **12** includes a burner and nebulizer mechanism **14** that nebulizes a sample and mixes the sample with fuel to create a flame **16** in the burner, which flame atomizes the sample. As in other conventional atomic absorption spectrophotometers, the flame **16** is irradiated by light from a source (not shown) having emission lines the same as the element being sought in the sample. The absorbance of light by the vaporized sample is related to the concentration of the element in the sample. The absorbance is measured and produces a graphical output on a recorder **18**. The recorder **18** may, for example, comprise a Model **165** Recorder manufactured by The Perkin-Elmer Corporation.

A gas generator accessory **20** is included in the apparatus **10** to extract in the form of a gaseous hydride an element from a group that includes arsenic and selenium. A sample that may for example contain a trace amount of arsenic is inserted into a reaction vessel or Erlenmeyer flask **22**. The reaction vessel **22** may for example be supported by a jack **24** that is mounted on a stand **26**. A dosing column **28** is inserted into the neck of the flask **22** and the dosing column **28** is supported on the stand **26** by means of a clamp **30** that is affixed to a support bar **31** rigidly mounted to the stand **26**.

An inlet tube **32** and an outlet tube **34** are connected to and supported by the dosing column **28** for carrying the gaseous hydride created in the generator **20** to the burner nebulizer **14** in the spectrophotometer **12**. Consequently the inlet tube **32** is coupled to an auxiliary source **36** of inert gas, such as argon. The inert gas is stored under pressure so as to carry the gaseous hydride out of the gas generator **20** and into the outlet tube **34**. The outlet tube **34** is coupled as diagrammatically indicated at **35** to the auxiliary oxidant tube **38** of the spectrophotometer **12**.

The inlet tube **32** and the outlet tube **34** support a stopcock assembly **40**. As shown more clearly in FIG. **2**, the stopcock assembly **40** includes a rotatable stopcock **42** having a pair of apertures **44** and **46** penetrating through the stopcock **42** transverse to the axis thereof. The apertures **44** and **46** are positioned in the stopcock **42** such that the aperture **44** aligns with the outlet tube **34** and the aperture **46** aligns with the inlet tube **32** when the stopcock is in the position shown in FIG. **2**. The stopcock **40** is mounted in a stopcock assembly housing **48** that is supported by the inlet and outlet tubes **32** and **34**. The stopcock **40** is held in the housing **48** by means of a washer **50** and stop nut **52** that fits the threaded end of the stopcock **40**. The stopcock **40** includes a handle **54** for rotating the stopcock **40** within the housing **48**. A bypass tube **56** interconnects the inlet tube **32** to the outlet tube **34** of the gas generator **20** when the stopcock **40** is rotated to close apertures **44** and **46**.

The dosing column **28** also includes a dosing stopcock assembly **60** which, includes a tapering stopcock **62** that contains a cavity **64** for storing a reagent therein. The cavity **64** is positioned such that when the stopcock **62** is inserted into the dosing stopcock housing **65**, the cavity **64** aligns itself with the dosing column **28**. The dosing stopcock **62** is held in the housing **60** by means of a washer **63** and stop nut **61** fastened to the threaded end of the stopcock **62**.

An elastic gas reservoir **70** is coupled to an apertured nipple **72** mounted in the dosing column **28**. Nipple **72** includes a plurality of circumferential ridges **74** for firmly holding the neck **76** of the elastic reservoir **70**. The elastic reservoir **70** may for example comprise a

resilient, expansible member that exhibits the capabilities of collecting and storing the gaseous hydride generated in generator **20.** The reservoir then expels the gaseous hydride when the inlet-outlet stopcock **42** provides a path to the spectrophotometer **12.** One elastic reservoir **70** utilized in practicing the invention was a latex balloon having a wall thickness of 0.012 inches.

Burner nebulizer **14** of the spectrophotometer **12** with hydrogen fuel derived from a source **80** coupled to the burner nebulizer **14** through a fuel line **82.** To provide an argon-hydrogen entrained air flame in the spectrophotometer **12** an argon source **84** is coupled to the nebulizer tube **86** of the spectrophotometer **12.**

OPERATION

In preparing a sample for atomic absorption spectroscopy, approximately 20 milliliters of the sample is pipetted into the reaction vessel **22.** The sample **23** should contain at least 0.01 micrograms of an element from the group including arsenic and selenium. In this description it is assumed that arsenic is the element contained in trace amounts in the sample. The next step in the gaseous hydride generation is the addition of concentrated hydrochloric acid of an amount sufficient to bring the sum of the sample and gas to 40 milliliters. A 1-milliliter volume of 20 percent stannous chloride solution is added to the reaction vessel **22** and allowed to stand for several minutes after thorough mixing. The next step in the generation of the gaseous hydride is the connection of the reaction vessel **22** to the dosing column **28.** The support jack **24** may for example be lowered and raised such that there is easy insertion and removal of the reaction vessel **22** into the dosing column **28.** Approximately 1.5 grams of meshed zinc metal is inserted into the open neck of the dosing column **28** for storage in the cavity **64** of the dosing stopcock **62.**

The inlet-outlet stopcock **42** is then rotated to connect the upper portion of the inlet tube **32** to the lower portion thereof as well as to connect the upper portion of the outlet tube **34** to the lower portion thereof. The auxiliary source **36** of argon therefore flushes out any oxygen contained in the reaction vessel **22** as well as in the rest of the system **10** and causes this oxygen to be burned in the flame **16.** Such oxygen would impede the formation of the gaseous hydride if allowed to remain in the system **10.** The inlet-outlet stopcock **42** is then rotated to displace the apertures **44** and **46** from the inlet and outlet tubes **32** and **34** to effectively seal off the reaction vessel **22** from the spectrophotometer **12.** The dosing stopcock **62** is then rotated to cause the zinc contained in the cavity **64** thereof to drop into the sample acid mixture in the reaction vessel **22.** The zinc reacts with the hydrochloric acid in accordance with the chemical equation:

$$2HCl{=}Zn \rightarrow H_2{+}ZnCl_2 \qquad (1)$$

The hydrogen released by this reaction then reacts with the arsenic in the sample to form arsine gas in accordance with the formula:

$$2As{+}3H_2 \rightarrow 2AsH_3 \qquad (2)$$

as well as free hydrogen gas.

The free hydrogen gas as well as the arsine gaseous hydride created in the reaction vessel **22** flows into and expands the elastic reservoir **70** because the gas generator **20** is gas tight at this time. The reservoir **70** expands to store the gaseous hydride under pressure. At the end of this reaction, which is allowed to continue for approximately 4 minutes, substantially all of the arsenic in the sample has been turned into a gaseous hydride and is stored in the expansible reservoir **70.** At this time, the inlet-outlet stopcock **42** is rotated to connect the gas generator **20** with the spectrophotometer **12.** The auxiliary argon gas **36** therefore sweeps into the gas generator **20.** The reduction in pressure in the gas generator **20** causes the elastic reservoir **70** to release the entrapped gaseous hydride and excess hydrogen gas and the argon stream flowing into the gas generator **20** from the argon source **36** sweeps the gases into the outlet tube **34.** The gaseous hydride is therefore carried to the burner nebulizer **14** and atomized in the flame **16.** A spectrophotometric examination is made of the element in the flame **16.**

The extraction of minute traces of arsenic from the sample and their detection in the atomic absorption spectrophotometer **12** is made feasible by concentrating the arsine gas in the reservoir **70** and then releasing this concentration very rapidly into the burner nebulizer **14.** In FIGS. **5** and **6** there are shown recordings of the detection in samples of 0.1 and 0.2 micrograms of arsenic and selenium respectively, with the absorbance measured and recorded by the recorder **18.** It is to be noted that such submicrogram traces of arsenic and selenium are detectable in the sample.

In FIGS. **3** and **4** there are shown the recorder tracings for solutions containing 0.5, 1, 1.5 and 2 micrograms of arsenic and selenium respectively. It is to be noted that the gaseous hydrides generated produce increasingly discernible spikes in the output provided by the recorder **18.**

It appears that any element capable of forming a gaseous hydride such as antimony and bismuth is detectable in the gas generator **20** in addition to arsenic and selenium. Furthermore any element amenable to atomic absorption spectroscopy that can be converted to any gaseous compound is analyzable by the apparatus **10.** Additionally the flame **16** is only one means of dissociating the metal hydride formed. Other means are a thermal furnace, an electrical furnace and the like.

Thus in accordance with the invention a gas generation accessory is provided for an atomic absorption spectrophotometer that permits samples containing trace amounts of particular elements that can be converted into gaseous compounds to be readily analyzed in the atomic absorption spectrophotometer. This is accomplished by extracting the elements from the sample to create the gaseous compound in an elastic reservoir and then expelling the stored gaseous compound into the flame of the spectrophotometer in a very short space of time. Such a projection produces a spiked output in the spectrophotometer which is readily discernible above the baseline fluctuation of the spectrophotometer.

What is claimed is:

1. The method of analyzing in an atomic absorption spectrophotometer a sample containing an element from a group consisting of arsenic and selenium, comprising the steps of:

adding an acid to said sample in a reaction vessel,
purging said reaction vessel with an inert gas to remove oxygen from said vessel,
reacting a metal with said acid to release hydrogen gas,
closing off said reaction vessel during said reaction,

collecting in an elastic reservoir a gaseous hydride that is created by the reaction of said hydrogen gas with said element,
opening said reaction vessel at the end of said reaction so as to permit said elastic vessel to expel said gaseous hydride to said spectrophotometer to project a concentrated amount of said element in the form of a gaseous hydride into said spectrophotometer in a short space of time.

2. The method as claimed in claim **1** wherein said acid comprises hydrochloric acid and said metal comprises zinc.

3. A gas generation accessory for an atomic absorption spectrophotometer comprising, in combination:
a reaction vessel adapted to contain an acid and a sample to be analyzed;
a dosing column coupled to said vessel for introducing a granular metallic reagent into said vessel;
an elastic expansible reservoir coupled in a gas-tight relation to said vessel for collection and storage under pressure of gaseous reaction products generated in the vessel;
conduit means for conducting gaseous generation products from said vessel and reservoir to an atomic absorption spectrophotometer; and
means for releasing such reaction products after generation thereof from said vessel and expansible reservoir to said conduit means.

4. An accessory according to claim **3,** wherein said conduit includes an inlet tube for connection to a source of purging gas under pressure and an outlet tube for connection to the spectrophotometer.

5. An accessory, according to claim **4,** including:
a bypass conduit interconnecting said inlet and outlet tubes and, shunted across the bypass conduit at a location between the bypass conduit and the reaction vessel, multi-position valve means adapted in one position to permit flow through said inlet and outlet tubes into and out of said vessel and, in another position, to restrict flow in said inlet and outlet tubes to said bypass conduit.

* * * * *