

[72] Inventors **Vernon A. Stenger;**
David N. Armentrout, both of Midland,
Mich.
 [21] Appl. No. **8,545**
 [22] Filed **Feb. 4, 1970**
 [45] Patented **Sept. 21, 1971**
 [73] Assignee **The Dow Chemical Company**
Midland, Mich.

[54] **METHOD AND APPARATUS FOR THE**
DETERMINATION OF PHOSPHORUS IN AQUEOUS
SOLUTIONS
17 Claims, 2 Drawing Figs.

[52] U.S. Cl. **23/230 R,**
23/230 PC, 23/232 E, 23/253 R, 23/253 PC,
23/254 E
 [51] Int. Cl. **G01n 31/12**
 [50] Field of Search. **23/230,**
232, 253, 254

[56] **References Cited**
UNITED STATES PATENTS
 3,423,181 1/1969 Dimick et al. 23/254

OTHER REFERENCES

Bernhart et al., "Flame Photometric Determination of Phosphorus in the Presence of Sodium, Potassium, and Other Cations," Analytical Chemistry Vol. 33, No. 3, Mar. 1961 pp. 395-396.

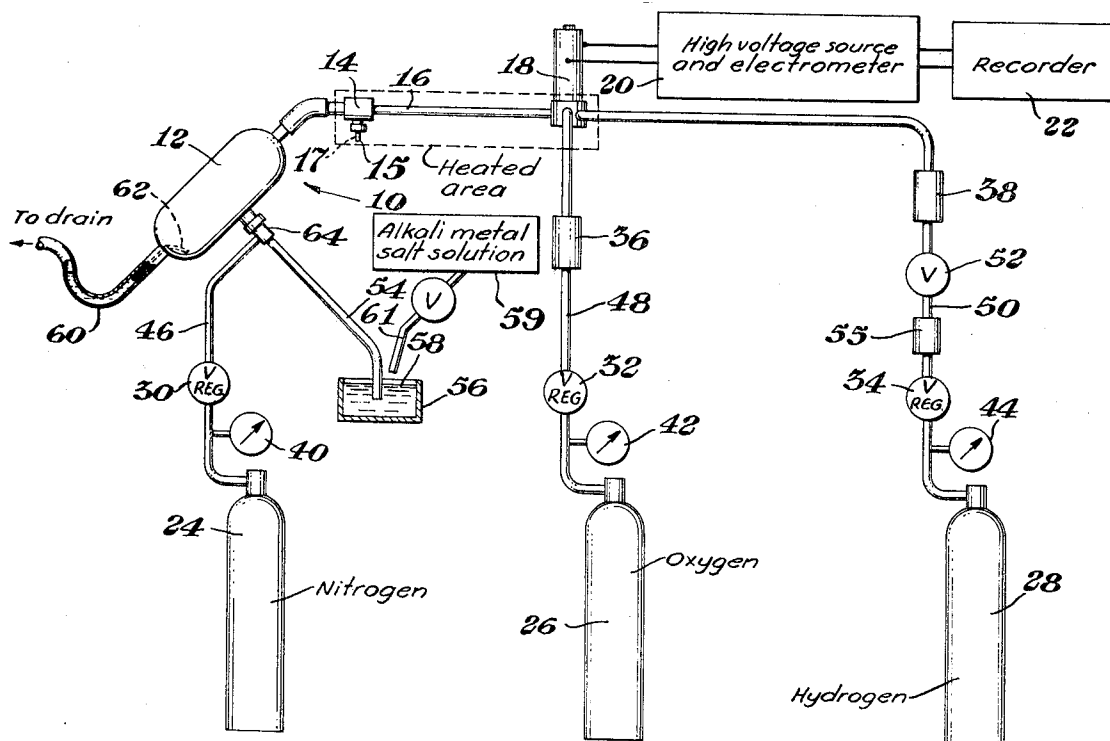
Page et al., "Mechanism of the Determination of Phosphorus With a Flame Ionization Detector," Analytical Chemistry, Vol. 40, No. 1, Jan. 1968 pp. 210-212.

Primary Examiner—Morris O. Wolk

Assistant Examiner—R. E. Serwin

Attorneys—Griswold & Burdick and Earl D. Ayers

ABSTRACT: A method and apparatus for directly determining inorganic phosphorus in water samples, comprising adding a very small amount of an alkali metal salt to the water solution containing the phosphorus compound, atomizing the water solution pneumatically, injecting the atomized particles into a flame ionization detector where interaction between the alkali metal and the phosphorus produces in the flame an enhanced ionization that is proportional to the phosphorus concentration.



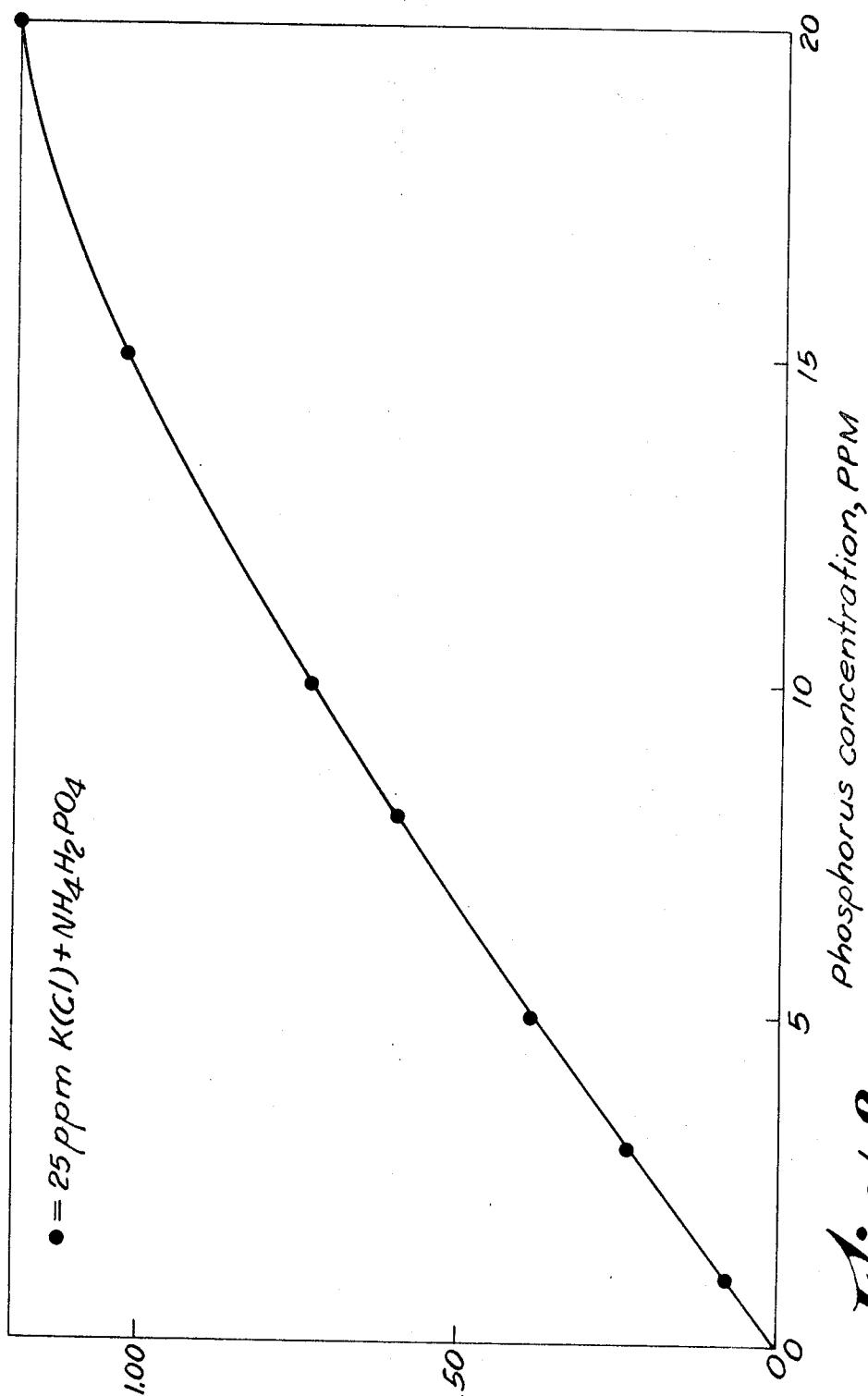


Fig. 2

signal millivolts

INVENTORS.
 Vernon A. Stenger
 BY David N. Armentrout
 Earl D. Ayers
 AGENT

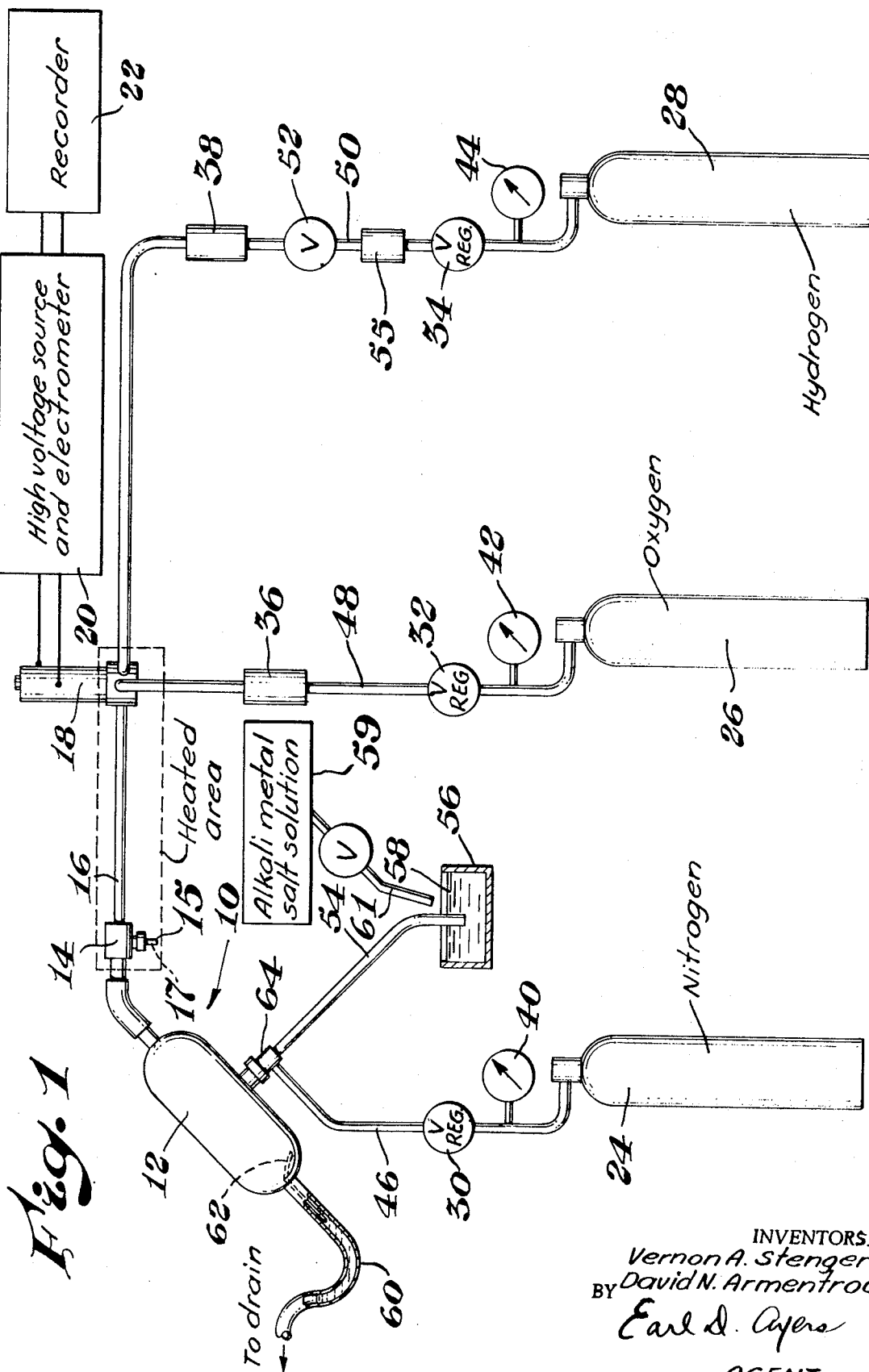


Fig. 1

INVENTORS.
 Vernon A. Stenger
 BY David N. Armentrout
 Earl S. Ayers
 AGENT

METHOD AND APPARATUS FOR THE DETERMINATION OF PHOSPHORUS IN AQUEOUS SOLUTIONS

BACKGROUND OF THE INVENTION

This invention relates to a method and apparatus for determining inorganic phosphorus in water solution and particularly to such a method and apparatus wherein a flame ionization detector is used.

An "alkali" flame ionization detector (FID) has been used to detect phosphorus-containing organic compounds eluting from a gas chromatographic column, but it is impossible to vaporize inorganic phosphates and detect them with the reported detectors.

Accordingly, it is a principal object of this invention to provide an improved method and apparatus for directly determining the amount of inorganic phosphorus in aqueous solutions.

Another object of this invention is to provide an improved, easier to use accurate method and apparatus for directly determining the amount of inorganic phosphates in aqueous solutions.

In accordance with this invention, a low concentration of an alkali metal salt is added to the water solution containing the phosphorus compound and the water solution is atomized pneumatically. The aerosol is then carried into a flame ionization detector where interaction between the alkali metal and the phosphorus species produces in the flame an enhanced ionization which is proportional to the phosphorus concentration (usually in the range of 0.1 to 20 parts per million) in the water sample. The signal from the detector is then amplified and recorded.

The invention, as well as additional objects and advantages thereof will best be understood when the following detailed descriptions are read in connection with the accompanying drawings, in which:

FIG. 1 is a diagrammatical view showing apparatus in accordance with this invention; and

FIG. 2 is a graph showing magnitude of electrical output signal of the flame ionization detector as a function of phosphorus concentration.

Referring to the drawings, particularly to FIG. 1, there is shown apparatus for determining the concentration of phosphorus in water solutions in which there is introduced to an ionization chamber 12 atomized phosphorus solution 58 to which has been added a low concentration of an alkali metal salt, such as potassium chloride, for example, from the source 59 through valved tube 61 from a suitable container 56 for the mixture.

Pressurized nitrogen from the tank 24 is coupled through line 46 having a pressure-regulator valve therein and a pressure gauge coupled thereto to an atomizer comprising a Beckman-type atomizer-burner 64 as used in flame emission and atomic absorption work. The sample material 58 is coupled to the aspirator 64 through tube 54.

The enclosed hollow chamber 12 has a drain end through which condensed sample material flows into a drain tube 60, usually through a wick 62 which extends from the bottom of the chamber 12 into the tube 60.

Atomized sample is conducted from the upper or output end of the chamber through a T-joint 14 and tube 16 by means of suitable coupling such as a silicone rubber tubing, for example, to a flame ionization detector 18 to which is electrically coupled a high-voltage source and electrometer 20 to provide an electrical output signal. A suitable recorder 22 or other readout device is coupled to the electrometer. Excess atomized sample from the output of the chamber 12 is removed through a bypass tube 15 extending from the T-joint 14 and having a suitable orifice 17 in its wall.

Oxygen from pressurized source 26 is coupled through line 48 having a pressure regulator 32 and flowmeter 36 therein and gauge 42 coupled thereto to another input of the flame ionization detector 18.

Hydrogen from a pressurized source 28 is also coupled to an input of the flame ionization detector 18 through line 50 hav-

ing a pressure regulator 34, needle valve 52, and flowmeter 38 therein and a pressure gauge 44 coupled thereto.

In operation, water samples containing inorganic phosphates, for example, which are freed from significant interfering substances, are treated with an alkali metal salt such as potassium chloride, for example, and aspirated into a suitable flame ionization detector, such as a Wilkins Aerograph flame ionization detector, for example.

The inorganic phosphate species enhance the potassium ionization in the flame proportionally to the phosphorous concentration of the solution.

Interfering cations may be removed from sample phosphate material by either of two procedures, for example. One procedure makes use of ion exchange and the other procedure involves converting the phosphorus to orthophosphate and precipitating it with quinoline molybdate. The precipitate is then washed and redissolved for analysis.

Nitrogen pressure used to aspirate the sample material is usually about 14 pounds per square inch, while flow rates of 300 milliliters per minute of oxygen and 17 milliliters per minute of hydrogen are usually supplied to the flame ionization detector 18. A flow restrictor 55 is usually also incorporated into the line 50, and may be a standard aerograph hydrogen flow restrictor, for example.

Usually hole(s) are provided in the cylinder cap of the detector 18 to permit combustion gases to escape.

A Sargent Model SR recorder or equivalent, 1.0 millivolt full scale and 0.5 inch per minute chart speed have been used as the recorder 22.

The T-joint 14, bypass tube 15, and tube 16, usually copper, are heated during operation of the apparatus, as by electrical heating tape, for example.

The atomizer may be a Beckman No. 4020 atomizer-burner, for example.

It has been found in one apparatus used that only about 1.8 percent of the nitrogen flow enters the detector 18. The remainder escapes through the orifice 17 in the bypass tube 15. However, other proportions may be used in other setups.

Studies were undertaken to optimize the various parameters for the measurement of 0 to 20 p.p.m. phosphorus in water. The more important variables studied were alkali salt composition and concentration and gas compositions and flow rates.

The salts tested with phosphate standards were sodium, potassium, rubidium, and cesium chlorides. Potassium was judged the best cation because of its large signal with phosphorus compared to sodium, the stability of the signal and less interferences compared to cesium, and its ready availability compared to cesium and rubidium. The rubidium response appeared about equivalent to potassium.

Table I shows the results of a study to determine the optimum potassium concentration in a 10 p.p.m. phosphorus standard. The total signals observed were divided into the contributions from the potassium background thermal ionization and the potassium ionization due to the phosphorus species.

TABLE I

EFFECT OF POTASSIUM CONCENTRATION ON THE PHOSPHORUS RESPONSE

Potassium conc., p.p.m.	signal, divs.	Signal with Added Phosphate (10 p.p.m. P)	
		total, div.	due to P, div.
5	1	32	31
10	2	60	58
25	6	71	65
50	12	76	64
100	17	88	71
200	42	112	70

The potassium background signal is directly proportional to the potassium concentration, but the signal due to phosphorus does not increase significantly for potassium concentrations above 25 p.p.m. potassium. All further work was done with 25 p.p.m. potassium.

Several gases for atomizing the sample and supporting combustion in the flame ionization detector were evaluated. The largest signals were observed with nitrogen for atomization and oxygen to support combustion. With a mixture of 80 percent argon and 20 percent oxygen instead of pure oxygen, a more linear phosphorus analytical working curve resulted. However, the improvement was not significant enough to justify use of the mixture.

Dependence of the potassium background and phosphorus signals on the hydrogen flow rate has been demonstrated in our tests. The background ionization from 25 p.p.m. potassium continuously increases with increasing hydrogen flow while the signal due to the phosphorus reaches a maximum at 16.8 ml./min. The flow rate should be controlled at 16.8 ± 0.5 ml./min. to obtain a stable maximum response. When the nitrogen flow rate was increased and the hydrogen flow optimized, larger signals resulted but the ratio of phosphorus signal to the background did not improve. The Beckman atomizer was operated at a nitrogen pressure of 14 p.s.i., to provide the most efficient atomization, and the nitrogen flow to the detector was controlled by the size of the bypass orifice.

The instrument is equally responsive to phosphorus in all the inorganic phosphorus compounds that have been tested. These include pyrophosphate, tripolyphosphate, hexametaphosphate, and decapolyphosphate. The pH of the sample has no effect on the response.

To obtain the maximum instrumental response, the potassium and the phosphorus compound apparently must enter the flame chemically combined in a solid particle that remains after the solvent has evaporated. For example, when potassium and phosphate solutions were aspirated independently into the detector 18, the resulting signal was considerably less than when the potassium and phosphate were in the same solution.

It is believed the instrument can possibly be improved by using an atomizer assembly in which the sample is aspirated into a heated chamber where the solvent is vaporized. The vapor is condensed in a cold trap while the aerosol particles continue to the flame. Eliminating the water vapor from the nitrogen line would increase the long term stability of the detector.

The common ions which interfere with the measurement of phosphorus are sodium, calcium and sulfates, for example.

Referring now to FIG. 2, it may be seen that the graph shows the output signal received when inorganic phosphates are present in a wide variety of concentrations at a given level of potassium chloride addition. While the graph is essentially a calibration curve, it has been found to be typical of the response of the method when used in connection with a great number of inorganic phosphates including polyphosphates.

We claim:

1. A method of determining the amount of inorganic phosphorus present in aqueous solutions, comprising mixing a predetermined amount of alkali metal salt material with said phosphorus containing solution, aspirating said mixture of

phosphorus solution and alkali metal salt, introducing said aspirated mixture into a flame ionization detector while feeding a predetermined amount of hydrogen and other combustion supporting gas material to said detector, and developing an electrical signal which is a function of the phosphorus in the flame of said detector.

2. A method in accordance with claim 1, wherein said phosphorus is in phosphate form.

3. A method in accordance with claim 1, wherein said alkali metal salt material is from the group consisting of potassium, rubidium and cesium halides, nitrates and acetates.

4. A method in accordance with claim 1, wherein said alkali salt is potassium chloride in between 5 and over 200 p.p.m. concentration in the mixture.

5. A method in accordance with claim 1, wherein pressurized nitrogen is used to aspirate said mixture and introduce it to said detector.

6. A method in accordance with claim 1, wherein air is used to aspirate said mixture and introduce it to said detector.

7. A method in accordance with claim 1, wherein said aspirated mixture is heated following its aspiration.

8. A method in accordance with claim 7, wherein water vapor is removed from said aspirated mixture before it enters said detector.

9. A method in accordance with claim 1, wherein the other gas material to support combustion is selected from the group consisting of oxygen or mixtures of oxygen and argon wherein argon is the major constituent.

10. A method in accordance with claim 1, wherein said phosphorus is present in amounts from 0.1 to about 20 p.p.m.

11. Apparatus for determining the amount of inorganic phosphorus present in aqueous solutions, comprising a source of phosphorus solution to be analyzed, means for adding a predetermined amount of alkali metal salt solution to said source, means for atomizing said combined phosphorus solution and said alkali metal salt solution, a flame ionization detector, means for introducing said atomized combined solutions to said detector, and signal readout means coupled to said detector.

12. Apparatus in accordance with claim 11, wherein a hydrogen source and combustion-supporting gas source are coupled to aid detector.

13. Apparatus in accordance with claim 11, wherein said means for atomizing said combined solutions comprises a mechanical aspirator having inputs and an output and a source of gas which is pressurized with respect to the output or said mechanical aspirator.

14. Apparatus in accordance with claim 11, wherein means are provided for heating said aspirated combined solutions before they are introduced to said detector.

15. Apparatus in accordance with claim 11, wherein means are provided for removing excess gas from said aspirated combined solutions before the combined solutions are introduced to aid detector.

16. Apparatus in accordance with claim 11, wherein the output of said means for atomizing is coupled to an expansion chamber.

17. Apparatus in accordance with claim 16, wherein means are provided in said expansion chamber for withdrawing water therefrom.