United States Patent

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[33] **Germany**
[31] **P 18 15 958.5**

[54] **METHOD OF AND DEVICE FOR THE MODULATED SAMPLE SUPPLY IN THE SPECTROCHEMICAL ANALYSIS OF A SOLUTION**
7 Claims, 5 Drawing Figs.

[52] **U.S. Cl.** **356/85,** 356/87, 431/1, 431/126
[51] **Int. Cl.** **G01j 3/00**
[50] **Field of Search** 356/85–87; 431/1, 126

[56] **References Cited**

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ABSTRACT: The invention relates to a method and a device used in the spectrochemical analysis of a solution in which samples of the solution are fed periodically from a sample vessel to a vaporizer to produce in the latter a photometric signal. The fluid line between the sample vessel and the vaporizer consists principally of flexible hoses and contains at least one section of a rigid capillary tube which by means of an eccentric drive mechanism is reciprocated lengthwise to its longitudinally axis to convey individual columns of the sample solution to the vaporizer.

The sample vessel may be divided into a plurality of sections, each containing a different solution and one end of the fluid line may be periodically immersed by the action of said eccentric drive successively into these sections to convey successively a different solution to the vaporizer.

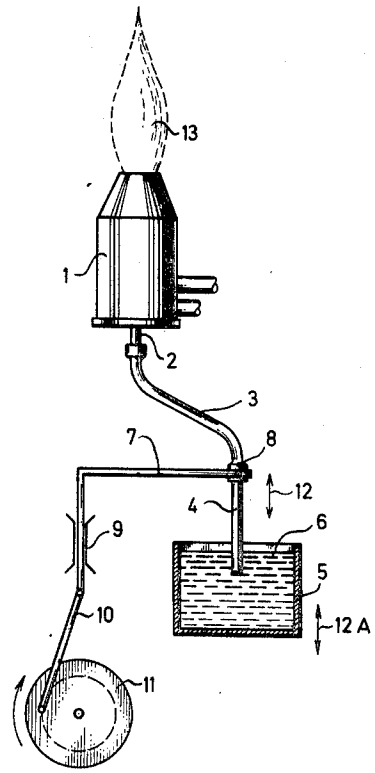


Fig.1

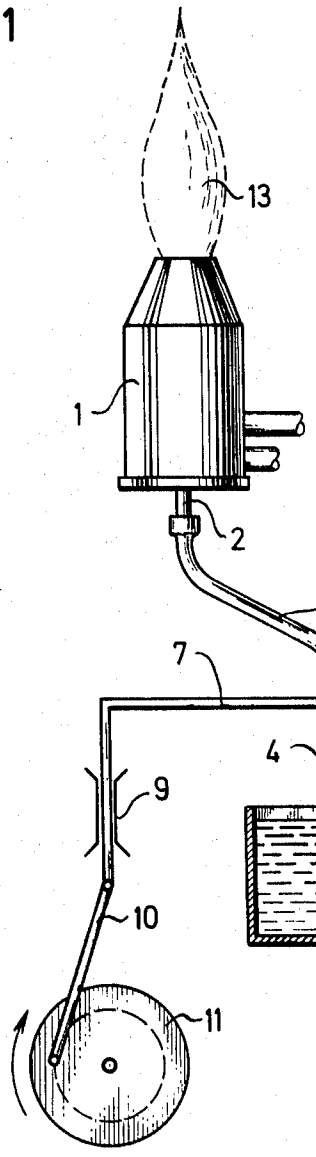


Fig.2

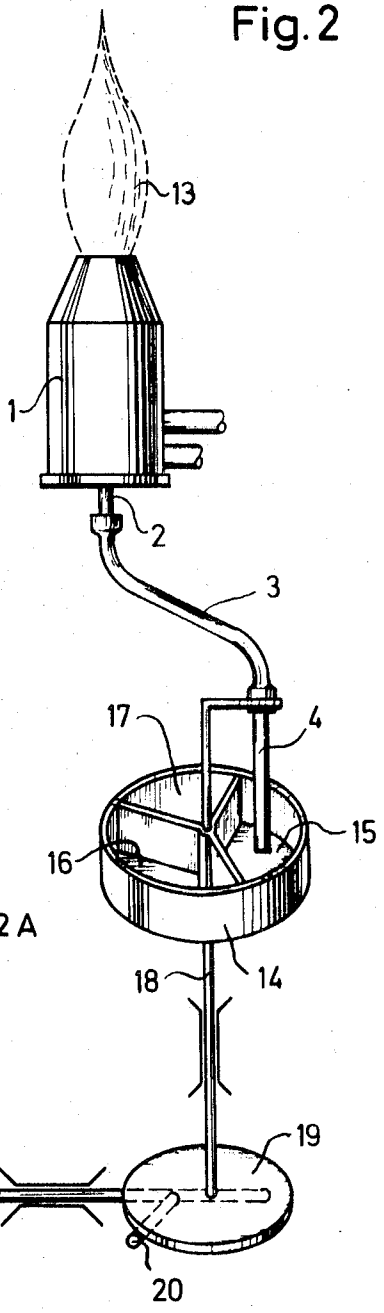


Fig.5

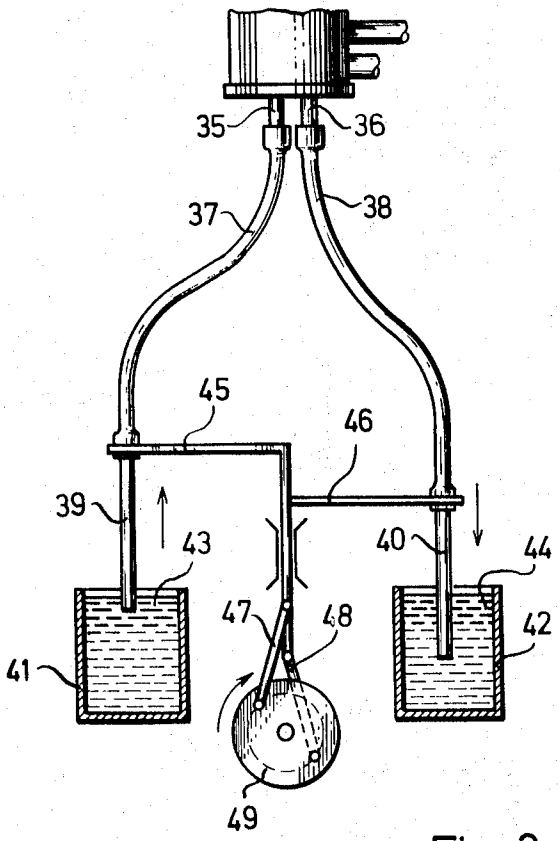


Fig.4

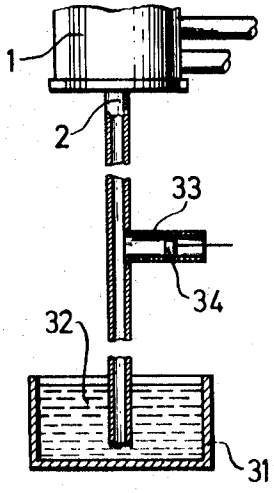
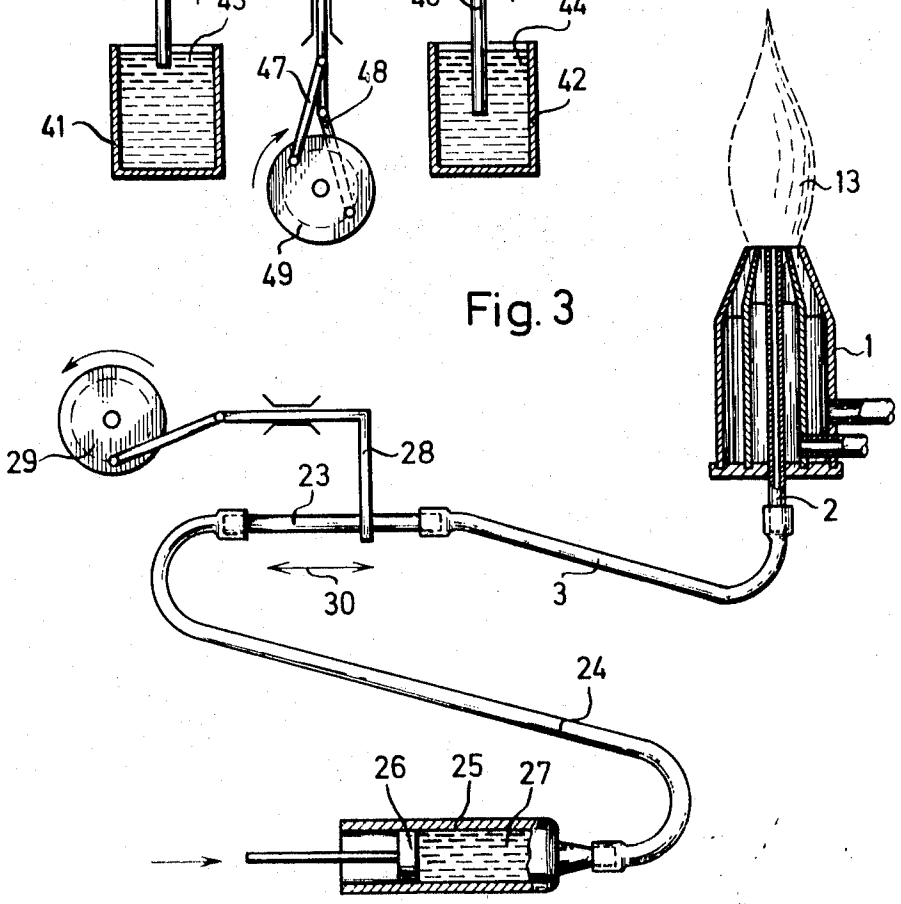


Fig.3



METHOD OF AND DEVICE FOR THE MODULATED SAMPLE SUPPLY IN THE SPECTROCHEMICAL ANALYSIS OF A SOLUTION

In methods of spectrochemical analysis of solid bodies, solutions and gases, it is desirable, particularly in trace analysis, to eliminate the background of a spectral line, if possible automatically. In order to solve this problem, it has been proposed to modulate the line intensity while leaving the background unmodulated, whereby the modulated alternating signal of the line can be separated from the direct light or direct current portion of the background by a simple AC measuring technique.

The modulation of the line intensity can be achieved by a modulated sample feed. In analytical methods operating by means of flames, the liquid injection into the flame, i.e. vaporization of the solution is modulated. Such a modulated vaporization is, however, not only interesting in analytical methods operating by means of flames, but is also of interest in other known spectrochemical analytical methods. Moreover, this method is not only of great interest in the emission analysis, but also in the absorption and fluorescence analyses.

The modulation of the sample feed may consist in that the solution under analysis is intermittently supplied to the vaporizer. It is, however, also possible and advantageous in many cases to have the analytical solution supplied to the vaporizer alternatingly with other solutions, for instance, alternatingly with the blind solution.

In the emission spectrochemical analysis the intermittent sample feed has certain specific advantages with respect to the elimination of the flame background. It is, however, likewise highly advantageous in the absorption spectrochemical analysis where it permits a more accurate determination of trace concentrations. This is possible, since the nonabsorbing adjacent lines of the background emitter are not modulated, while the absorbing resonance line creates alternating signals.

An alternating vaporization of analytical blind solutions permits the complete elimination of the flame background and is advantageous in all prior art analytical methods. It has already been proposed to eliminate the influence of radiation density variations by alternatingly vaporizing calibration solutions, blind solutions and analytical solutions.

It has also been proposed to use a hose pump for the intermittent sample feed and also for the alternating sample feed to the vaporizer. In the emission analysis, and also in the absorption and fluorescence analyses it has been found to be necessary to carry out the modulation of the sample feed at a frequency greater than 20 cycles. At lower frequencies the noise level is too great. It is advisable to operate in a frequency range of approximately from 20 to 50 cycles. Also higher frequencies are principally possible, but major technical difficulties are encountered in the realization of higher modulation frequencies. In the frequency range referred to as being advantageous the noise level remains almost constant.

Based on these investigations and considerations, one is forced to operate with relatively high interruption frequencies for the sample feed. In the mentioned recommended frequency range, the life of the hoses is substantially shortened when hose pumps are used. Furthermore, the internal diameter of the hoses changes during their short life, so that the integral sample feed changes relatively quickly with the passage of time. The integral sample feed should, however, remain constant during the time of observation of approximately 30 seconds.

The present invention now relates to a method of, and a device for the modulated sample feed in the spectrochemical analysis of a solution. It is an object of the method of the invention to carry out the modulation of the sample supply without the mechanical stress on the intake line, acting destructively in the recommended frequency range. Furthermore, the new modulation method is so performed that all demands from the measuring technique to be made on the modulated sample feed can be fulfilled. Finally, the new method is distinguished by the fact that a very simple device and an undisturbed operation of the device is possible for carrying it out.

According to the invention, the method of modulated sample feed in the spectrochemical analysis of a solution provides that at least one partial section of the line leading from the sample vessel to the vaporizer is periodically moved to and fro in an axial direction so that the liquid is permitted to pass the vaporizer only during a portion of its cycle of movement.

When the method of the invention is so performed that the free end of the intake or suction line is withdrawing from the solution during a portion of its cycle of movement, then individual liquid columns separated from each other by air columns will be established in the intake hose. These columns travel in the hose to the vaporizer and burner, respectively, at intake or suction speed. Thereat, flame photometric signals will be generated only when the liquid columns are vaporized, whereas approximately only the background will appear in the empty intervals, namely when air is supplied.

It is particularly advantageous to so perform the method of the invention that a partial section of the line leading to the vaporizer is moved in an axial direction during a portion of a cycle of movement at a speed which is greater than the velocity of flow of the solution in that section. By this measure, during movement of the partial section in a direction of flow, there will take place no feed of liquid to the vaporizer, whereas during the opposite movement of the partial section the feed of liquid will be greater than in the case of stationary hose.

During this performance of the new method, the inertia forces of the liquid are utilized and a splitting of the same into several liquid columns separated from each other is avoided, and a single incompressible liquid column remains in the intake hose. By this measure it is attained that the modulation of the sample feed is stable in frequency and phase and does not change with time.

It is advisable that in the described performance of the new method the free end of the intake line leading to the vaporizer is immersed in the solution during the whole cycle of movement and to periodically move this free end up and down.

In many cases, particularly when analyzing very viscous solutions it may also be advantageous to feed the solution to be vaporized into the line under pressure and to periodically move a section of the flexible intake line to and fro.

The object of the present invention is also attained by a method of modulated sample feed in the spectrochemical analysis of a solution, in which the volume of the line leading from the sample vessel to the vaporizer is varied periodically.

In the last described performance of the method of of the invention, utilizing the inertia forces of the liquid, primarily the requirements of a constant integral sample feed, of a modulation frequency greater than 20 cycles, of a best possible constancy of frequency and phase, and of a mark-to-space ratio as constant as possible can fully be complied with.

It is readily possible, with the new method to vaporize several solutions alternatingly. To this end, several intake or suction lines leading from different vessels to the vaporizer are moved with such a phase shift that only one respective solution is alternatingly fed to the vaporizer.

It is, however, also possible to alternatingly vaporize several solutions with one intake line only. For this purpose, the free end of this intake line is successively immersed in different solutions so that successive flows of liquid fed separated from each other by air columns travel in the intake line to the vaporizer.

The device according to the present invention is characterized by a particularly great simplicity. It comprises substantially a lever rocked by means of an eccentric drive as well as an at least partially flexible suction line to which the lever is so secured that a section of the line is periodically moved to and fro in an axial direction.

It is also possible to so construct the device that the intake line is provided with a lateral extension which is closed by a reciprocating piston or a vibrating diaphragm.

A few illustrative embodiments of the present invention will now be described in greater detail with reference to the FIGS. 1 to 5 of the accompanying drawing in which:

FIG. 1 illustrates a device for the intermittent vaporization of a solution;

FIG. 2 illustrates a device for the alternating vaporization of several solutions, using one intake line only;

FIG. 3 illustrates a device for the intermittent vaporization of a solution in which this solution is supplied to the vaporizer by a pump;

Flg. 4 illustrates a device in which the volume of the intake line is varied periodically; and

FIG. 5 illustrates a device for the alternating vaporization of two differing solutions, using two intake lines.

Referring to FIG. 1 the reference numeral 1 designates a prior art direct vaporizer-burner combination to which the solution to be analyzed is supplied by the capillary tube 2. A flexible capillary hose 3 to one end of which an additional capillary tube 4 is attached, is connected with its other end to the lower free of the capillary tube 2. The additional capillary tube 4 is immersed in the sample vessel 5 containing the solution 6 under analysis. The capillary tube 2, capillary hose 3 and additional capillary tube 4 preferably having all the same internal diameter.

An angular lever 7 has fixedly connected to one of its ends the lower end of the capillary hose 3 as at 8. This lever 7 is slidably supported with its vertical arm at 9 and is connected with its lower end to an eccentric rod 10. The rod 10 is pivotally connected with a drive disk 11 and is operated by the latter. When this disk rotates in a clockwise direction, the capillary hose 3 and thus the additional capillary tube 4 will be moved up and down in the direction of the double arrow 12.

In the embodiment illustrated in FIG. 1 the relations have been so selected that the lower end of the capillary tube 4 is lifted out of the analytical liquid 6 during one half of its cycle of movement. Therefore, in the capillary tube 2 individual liquid columns are separated from each other by air columns when fed to the flame 13. Accordingly, during the analysis are produced flame photometric signals only then when liquid columns are vaporized, where as the the flame 13 will burn empty when air is supplied.

The vessel 5 is preferably arranged for adjustment in height as indicated by the double arrow 12A. By this procedure, despite a lowering of the liquid level a corresponding adjustment can be obtained by a corresponding readjustment of the vessel 5, while on the other hand the level of the liquid may be changed for any other desired purpose. Thereby, an adaption of the modulation method to the different requirements is rendered possible in a simply manner.

The device illustrated in FIG. 1 can also readily be designed in such a manner that the capillary tube 4 remains in the solution 6 during the entire cycle of movement. In such a case, however, the capillary tube 4 and thus the intake opening for the feed of liquid is moved during the upward travel at a speed v_K which is at least equal to, or greater than the velocity of flow v_F of the solution in the intake line 2, 3, 4. There will be no feed of liquid through the capillary tube 4, as long as $v_K \geq v_F$ and both have the same sign. In case of v_K and v_F having opposite signs, the feed of liquid through the capillary tube 4 will be greater than if $v_K=0$. In the illustrated embodiment an intermittent vaporization is therefore obtained although one single incompressible liquid column is maintained in the capillary tube 2, 3, 4.

FIG. 2 illustrates a device for the alternating vaporization of several liquids and operating with a single intake line. The intake capillary tube 4 is immersed in a vessel 14 which is divided into three separate portions 15, 16, 17 by vertical partitions. These vessel portions may, for instance, contain a calibration, a blind and an analytical solution, respectively, or also may contain each a different analytical solution. The angular lever 18 which is connected with its upper horizontal arm with the capillary tube 4, passes with its vertical arm through the center of the vessel 14. The lower end of the lever 18 is fixedly connected with a horizontally disposed disk 19. A motor 22 drives a horizontal shaft 21 having thereon a lateral lever 20. Upon rotation of the shaft 21 this lever 20 is caused to engage the lower face of the disk 19. The disk 19 and with it the capillary tube 4 are lifted and at the same time rotated. Thus, the capillary tube 4 is successively immersed in the different vessel portions 15, 16, 17, whereby successive amounts of liquid are drawn from each vessel portion, which amounts of liquid are separated from each vessel portion, which amounts of liquid are separated from each other by air columns and travel through the intake line 4, 3, 2 to the direct vaporizer-burner combination 1.

In the embodiment of the invention illustrated in FIG. 3, the free end of a flexible hose 3 is connected with one end of the rigid capillary piece 23, while the other end of the hose 3 is connected with the intake capillary tube 2 of the burner combination 1. The other end of the said rigid capillary piece is connected with a pump 25 by a flexible hose 24. By movement of the piston 26 of this pump the solution under analysis 27 is conveyed into line 24, 23, 3, 2 uniformly and at a certain specific pressure. Under the influence of this pressure the liquid in the intake line flows at the velocity of flow v_F in a direction toward the burner combination 1. By means of the angular lever 28 operated by the eccentric 29, the capillary piece 23 is now moved to and fro in the direction of the double arrow 30. If the capillary piece 23 is moved at a speed of v_K from the left toward the right, which is at least equal to, or greater than the velocity of flow v_F of the solution in this capillary piece, there will be no feed of liquid through the capillary piece 23. Thus, in the illustrated example an intermittent vaporization is obtained, and one single incompressible liquid column is maintained in the intake line 24, 23, 3, 2, as has already been described in connection with FIG. 1.

In the device of the invention illustrated in FIG. 4, the intake capillary tube 2 of the burner combination 1 has been extended and its lower end is immersed in a vessel 31 containing the solution under analysis 32. The capillary tube 2 has between its ends a lateral extension tube 33 which is closed by a piston 34. The volume of the intake line is periodically varied by reciprocation of this piston 34. Thereby, a modulation of the sample feed is attainable and a single incompressible liquid column is maintained in the intake line.

In place of using the piston 34, one may also employ a diaphragm for closing the lateral extension tube 33. When this diaphragm is caused to vibrate, it will vary the volume of the intake line periodically, thereby effecting a modulation of the sample feed.

In the embodiment of the invention illustrated in FIG. 5 two capillary tubes 35 and 36 lead directly to a burner of the type illustrated in FIG. 3 or to a vaporizer chamber. Both capillary tubes 35 and 36 are preferably united by means of an inverse Y-piece to form one single short vaporizer capillary tube shortly before reaching the vaporizer tip. The mixing zone in the Y-piece should be kept small in comparison to the overall area of the liquid column in the intake hose.

The flexible capillary hoses 37, 38 are connected with the capillary tubes 35, 36. Additional extension capillary tubes 39, 40 are connected the hoses 37 and 38. The tubes 39 and 40 are immersed with their lower ends in the vessels 41, 42 containing the solutions 43, 44. The vessel 41 may, for instance, contain the analytical solution, while the vessel 42 may be filled with a blind solution. As to its composition this blind solution resembles the analytical solution, however, the concentration of the analytical element in it is zero. By way of example, it is also possible to fill a calibration solution into the vessel 41 and the analytical solution into the vessel 42. In that case, the photoelectric alternating signal will directly indicate the difference in the two concentrations.

Two vertically guided angular levers 45, 46 are fixedly connected with their horizontal arms to the upper ends of the vertically disposed capillary tubes 39 and 40. A drive disk 49 rotating in a vertical plane has on its front side an eccentric rod 47 pivotally connected and is attached with its upper end

to the lower end of the lever 45. On the rear of the drive disk 49 an eccentric rod 48 is pivoted whose upper end is connected to the lower end of the lever 46.

It will be noted that the tow levers 45, 46 and hence the capillary tubes 39 and 40 perform movements which are phase-shifted by 180°, so that an alternating vaporization of the solutions 43, 44 is obtained.

Principally, it is also possible to alternatingly vaporize more than two differing solutions with a device similar to that illustrated in FIG. 5. In such a case, however, provision must be made that the eccentric drives operate with such a phase shift that only one respective liquid will alternatingly be fed to the vaporizer.

What we claim is:

1. A method of modulated sample feed in the spectral analysis of a solution, including the steps of periodically moving to and fro in axial direction at least a section of a fluid line leading from a vessel which contains the solution to be analyzed to a vaporizer and at the same time subjecting said solution in said fluid line to a predetermined pressure while feeding it to said vaporizer, so that the solution will reach the vaporizer only during a portion of this to and fro movement, thereby causing an intermittent vaporization of said solution.

2. A method of modulated sample feed in the spectrochemical analysis of a solution, in which at least a section of a fluid line having a free end and leading from a sample vessel to a vaporizer is periodically moved to and fro in the axial direction of said section of said line, so that the solution will reach the vaporizer only during a portion of this cyclic movement, wherein the improvement comprises the steps of moving said section of the fluid line leading to said vaporizer in an axial direction during a portion of a cycle of movement with a speed which is greater than the velocity of flow of the solution in said section, and causing said free end of the fluid line to remain immersed in the solution during the entire cycle of movement.

3. A method as claimed in claim 2, additionally comprising alternatingly vaporizing several solutions by periodically moving several fluid intake lines leading from different sample vessels to said vaporizer, producing phase shift between the movement of said several intake lines whereby only one solution at a time will alternatingly enter said vaporizer.

4. A method of modulated sample feed in the spectrochemical analysis of a solution, including the steps of varying periodically the volume of the fluid line leading from a sample vessel to a vaporizer to vary the volume of solution fed to the vaporizer and maintaining a single uninterrupted liquid column in said fluid line.

5. A device for use in the spectrochemical analysis of a solution comprising vessel means for supplying a modulated sample to a vaporizer, including a pivotally mounted lever, an eccentric drive for operating said lever, a fluid intake line having a rigid section and at least one partially flexible section leading from said vessel means to said vaporizer, means for attaching said rigid section to said lever in such a manner that said rigid section of said fluid line is moved in an axial direction to and fro, wherein the improvement comprises a pump connected as said vessel means with one end of said fluid line for assuring a uniform supply of the solution, and said eccentric drive is said rigid section of said fluid intake line to move said rigid section connected to speed which is greater than the velocity of the flow of the solution in said rigid section.

6. A device for use in the spectrochemical analysis of a solution which feeds a modulated sample to a vaporizer, comprising a sample vessel and a vaporizer, a fluid intake line connecting said vessel with said vaporizer, said fluid intake line being provided with a lateral tubular extension independent if said vessel closed by means of a reciprocable member so as to vary, without interruption, the feed of the solution from said vessel to the vaporizer.

7. A device for used in the spectrochemical analysis of a solution comprising vessel means for supplying a modulated sample to a vaporizer, including a pivotally mounted lever, in eccentric drive for operating said lever, a capillary fluid intake line having a rigid section and at least one partially flexible section leading from said vessel means to said vaporizer, said rigid section being attached to said lever in such a manner that said rigid section of said fluid intake line is moved in an axial direction to and fro when said lever is actuated, wherein the improvement comprises a plurality of said capillary fluid lines leading to a single vaporizer, each of said lines being immersed and remaining immersed with one of their ends in a different solution for the alternating vaporization of several solutions a plurality of said levers operatively connected to said lines for periodically moving the same, and a plurality of said eccentric drives coupled to provide said lines with a phase shift such that only one solution at a time is alternatingly fed to said vaporizer.

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