Jan. 22, 1963 D. EXLEY 3,074,309

FLAME SPECTROPHOTOMETRY

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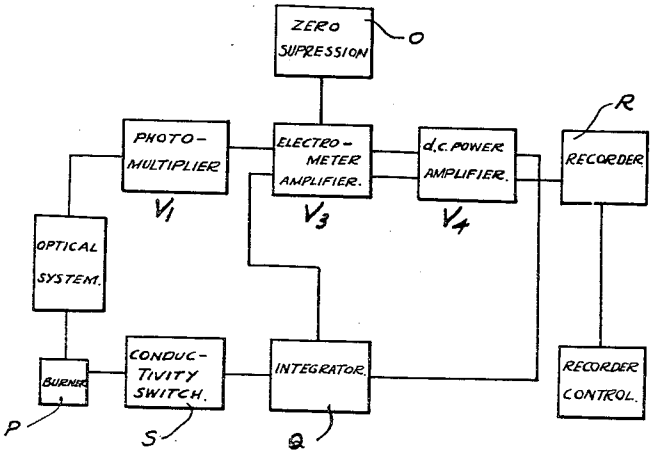
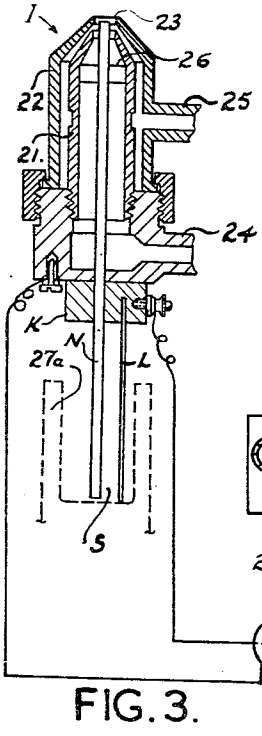


FIG. 1.



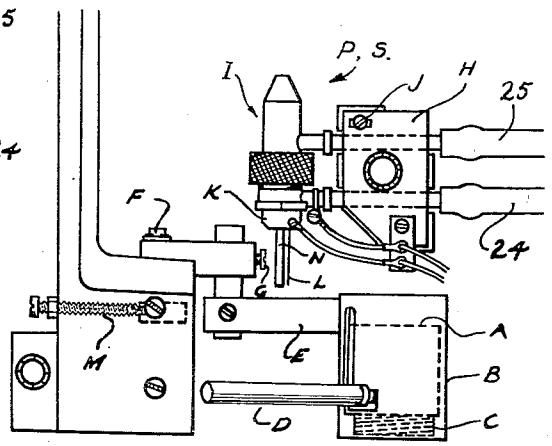


FIG. 2.

FIG. 3.

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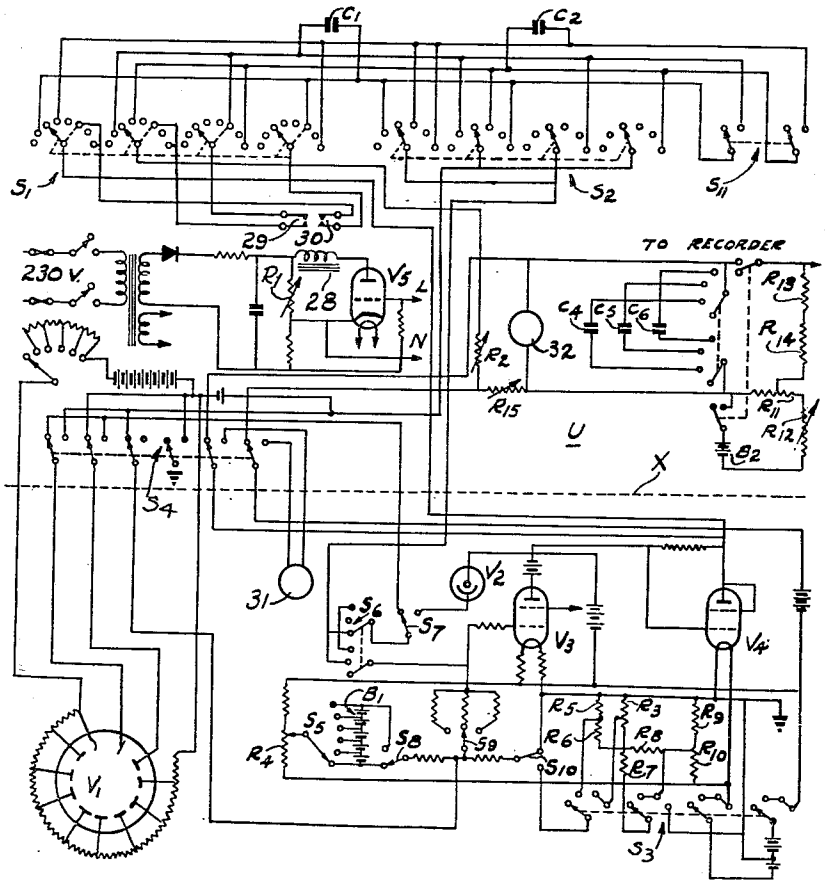
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FIG. 4.



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FLAME SPECTROPHOTOMETRY

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6 Claims. (Cl. 88—14)

This invention relates to flame spectrophotometry and has for an object to provide an instrument of high sensitivity capable of the detection and quantitative estimation of minute quantities of inorganic substances in solution—for example quantities which are of the order of three to four orders of magnitude less than the practical lower limits of response of normal commercially available instruments. The invention is primarily but not exclusively applicable to the detection or estimation of traces of inorganic matter in organic material such as biological fluids.

Apparatus constructed in accordance with the present invention has been successfully used to detect 3×10^{-13} gm. of sodium and 1×10^{-10} gm. of magnesium and to estimate quantitatively amounts of magnesium as low as 1×10^{-9} gm.

When detecting or estimating such minute quantities of inorganic matter by flame spectro-photometry, the background light from the flame tends to mask completely the weak wanted signals which are produced, whilst interference from other and unwanted constituents of the combustible mixture introduces further sources of error.

It is an object of the present invention to provide a method of detecting or estimating traces of a substance which consists in making a solution of said substance in an electrolyte, aspirating said solution through a burner and simultaneously causing said electrolyte solution to complete an electrical circuit to an integrator and integrating the light from said burner so long as said electrolyte solution maintains said electrical circuit.

Another object is to feed to the burner, in succession, equal volumes of electrolyte solution with and without said trace substance, respectively, and to compare the outputs of the integrator.

In a flame spectrophotometer according to the present invention, therefore, a solution of the wanted substance is aspirated into the flame by a burner which incorporates a conductivity switch. This switch relies on the presence of an electrolyte at the inlet to the aspiration tube or duct, the electrolyte constituting the sample solution, and triggers an electronic integrating circuit which integrates the output from a photoelectric flame detector of conventional type.

Preferably, the switch consists of an electrically conducting aspirator tube mounted in the burner so as to dip into the sample solution, and an adjacent electrode insulated from the aspirator tube and arranged to dip into the same solution at least to the same depth as the aspirator tube.

The integrator circuit conveniently consists of a condenser and suitable charging and discharging circuits, the latter including a detector—such as a galvanometer—or a recorder.

Advantageously, two condensers are arranged to be charged, respectively, by successive outputs from the photoelectric flame detector when first "blank" and then standard or sample solutions of equal volume are aspirated into the flame. The condensers are then discharged simultaneously in opposition through an indicating or recording instrument.

The invention can be applied to a commercially available spectrophotometer and, by suitable switching arrangements, the latter can optionally be used alone as an absorptiometer in the usual way without affecting its sensitivity or normal performance.

A preferred embodiment of the invention will now be particularly described, by way of illustration only, with reference to the accompanying drawings in which:

FIGURE 1 is a block diagram of the optical and electrical circuits;

FIGURE 2 is a side elevation of a burner assembly incorporating a conductivity switch;

FIGURE 3 is a sectional elevation of the burner proper of FIGURE 2; and

FIGURE 4 is a detailed circuit diagram of a flame spectrophotometer according to the present invention.

Referring first to FIGURE 1, the block diagram illustrates a photometer circuit consisting of a burner P for producing the desired spectrum which is viewed by a photo multiplier tube V_1 the output of which is amplified in two stages V_3, V_4. The output from the second of these stages, V_4, can be fed to an indicating or recording instrument if desired, but according to the present invention it is fed to an integrator Q which is triggered by a conductivity switch S incorporated in the burner assembly itself. This switch functions to energise the integrator Q automatically at the instant when a known or unknown substance is introduced into the flame, by the actual presence of the substance itself at the burner P, and similarly to de-energise the integrator when the substance ceases to be fed to the flame. Thus, the response of the phototube V_1 to the spectrum of the substance is integrated over the exact total period of its presence in the flame.

The output of the integrator Q is then amplified—in FIGURE 1 the same two stages V_3 and V_4 are used for this purpose by appropriate switching not indicated in the diagram—and the amplified integrator output is fed to the recorder R (or indicating instrument). As will be explained more fully below, this integration step enables a very weak signal, which is present for a very short period of time, to be accurately observed, due to the automatic timing of the period of integrator operation.

A zero suppression circuit 0 is shown coupled to the first amplifier stage V_3, the function of which is to suppress the amplifier response to the general background illumination from the flame (with solvent) which, when the wanted signal itself is very weak, would otherwise swamp the final output.

The conductivtiy switch S is shown in more detail in FIGURES 2 and 3. The substance to be introduced into the flame is dissolved in an accurately known volume of solvent and is introduced by expiration due to the venturi action of the burner. The solution to be aspirated is placed in a small cup or like vessel 27 (FIG. 3) which in turn is placed in a holder shown dotted at A in FIGURE 2. This holder is mounted in a cup positioner B capable of being swung into and out of its operative position immediately below the burner nozzle I, and is spring

loaded upwards by a helical compression spring C. The cup holder A is controlled by a handle D secured thereto and projecting through a bayonet slot in the side wall of the positioner B. The handle D also serves for swinging the positioner into and out of its operative position. The whole cup mounting assembly A, B, C is carried on a bracket E which is adjustable for height in a pivoted arm F, a clamping screw G serving to lock the assembly in the desired position of height adjustment.

The burner nozzle I is supported by a mounting block H of insulating material, this block being capable of small angular adjustment about a horizontal axis for permitting proper alignment of the burner flame with respect to the optical system, a set screw and slot arrangement J serving to lock the nozzle I in its position of alignment.

To the lower end of the nozzle is secured an insulating block K which carries a downward projecting electrode L, preferably of platinum, which constitutes one electrode of the conductivity switch S (FIG. 1) and is adapted to dip into the solution to be aspirated through the burner nozzle I when the cup **27** containing the solution is correctly positioned by the assembly A . . . G described above. This position is determined by an adjustable stop M on the frame of the burner housing and also by the handle D when it is moved in its bayonet slot to allow the cup holder A to rise, under the action of the spring C, until arrested by the end of the slot. The platinum electrode L is insulated by the block K from the nozzle I the body of which is in electrical contact with the aspirator tube N through which the solution to be analysed is introduced into the flame. This tube terminates at its lower end slightly short (say, by a distance of 1/32 inch) of the lower end of the insulated electrode L.

FIGURE 3 shows in greater detail the construction of the nozzle I. For the most part, it is of conventional pattern, consisting of concentric tubes **21**, **22** which taper at their upper ends to form a mixing nozzle **23**. Combustion gases are supplied under pressure through respective pipes **24**, **25** to the interiors of the two tubes, whilst through the centre of the inner tube **21** passes the metal capillary aspirator tube E. A spider **26** serves as a steady for locating the upper end of the tube N centrally in the nozzle **23**.

The working position of the cup **27** containing the solution to be aspirated is shown in dotted lines at **27***a*. It will thus be seen that the solution in the cup **27** bridges the gap between the aspirator tube N and the insulated electrode L to provide a conducting path between them. This path is only completed when the cup **27** is raised sufficiently by the spring C, and is broken as soon as all the solution has been aspirated. The electrode L and capillary tube N thus form an automatic switch S for controlling an external circuit.

The external circuit is a relay consisting of a hard triode V_5 in the anode circuit of which is an electromagnetic relay **28** having two pairs of contacts **29**, **30**. The electrode L and the burner nozzle I are connected across the grid and cathode of V_5 to control the conductivity of the triode, and hence the operation of the relay **28**.

The circuit of FIGURE 4 shows the modifications and additions to the circuit of a standard Beckman DU flame spectrophotometer, in accordance with the present invention. The circuit U above the dotted line X is that which has been added in order to introduce the automatic aspirator switch S and integrator Q of FIGS. 1–3.

The triode V_5 is shunted by a variable resistance R_1 which is set to ensure that the triode is normally non-conducting. When the electrode L and aspirating tube N (FIGS. 2 and 3) are short-circuited by the electrolyte solution in the cup **27**, V_5 becomes conducting and the relay **28** closes its contacts **29**, **30** to charge the integrating condenser C_1 or C_2 according to the settings of two multi-contact switches S_1 and S_2. Both condensers are charged from the amplifier stage V_4 through a variable resistance R_2 the setting of which is adjustable, depending on aspirating time at the burner nozzle I, so that only about 20% of the available charging voltage is reached in the selected condenser C_1 or C_2 to ensure that the voltage/time characteristic is substantially linear.

In a circuit which has been used for the estimations mentioned earlier, the condensers C_1 and C_2 were 8 μf. matched low leakage paper type rated at 25 volts working. With a medium bore capillary aspirating tube N, in a burner to which the combustible mixture supplied through the pipes **24**, **25** (FIGS. 2 and 3) was oxygen at 15 lb./in.^{2} and hydrogen at 3 lb./in.^{2}, 100 μl. of electrolyte solution including an enhancing solvent at 85% acetone and 5% HCl was aspirated in 3.5 seconds, and the value of R_2 was adjusted to 2M Ω. The cup **27** was of glass treated with a proprietary silicone fluid to reduce surface tension effects on the aspirated solution.

A brief description of the whole circuit is as follows:

The original instrument consists of the photomultiplier V_1, the red photocell V_2, the electrometer and amplifier valves V_3 and V_4 and their associated circuitry. The photomultiplier current is measured by balancing the voltage drop across the photomultiplier load resistor selected by a switch S_9 against the voltage across a potentiometer resistor R_3 (the so-called transmission dial) with the aid of the milliammeter **31** and the action of the amplifiers. A variable voltage, controlled by a potential divider R_4 and a switch S_5 connected across a battery B_1, is used to back-off the photomultiplier dark current and the signal produced by the flame background. A two-position switch S_7 selects either the photomultiplier V_1 or the red photocell V_2, whilst a similar switch S_{10} is coupled with a shutter (not shown) which, in the "off" position, prevents light from reaching the phototubes V_1, V_2 and is used for dark current compensation. The resistive network R_3 and R_5–R_{10} consists of the sensitivity control resistor R_{10} which, together with its series resistor R_9 controls the voltage across the transmission dial resistor R_3; and R_5 and R_6, which were chosen to give a 10:1 ratio (910+91) to provide a tenfold extended scale for R_3. The switch S_3, which has four positions (off, check, 1.0 and 0.1), controls the filament heating of the amplifiers V_3 and V_4, provides the correct condition for balancing the voltage across R_3 for 100% transmission without the need to set it for each reading, and finally provides normal and extended scales on which to balance the signal.

New switches S_4, S_6 and S_8 are incorporated in the Beckman circuit. Operation of S_4 enables a reversible potential to be applied across the anode load of the amplifier V_4. In the position of this switch as shown in FIGURE 4, a galvanometer **32** can be used in conjunction with a pen recorder (not shown) for integrating or direct reading purposes. The other position brings the original milliammeter **31** into circuit and enables the Beckman DU spectrophotometer to be used for absorption measurements, or normal flame spectrophotometry. S_8 was incorporated in order to reverse the polarity of the zero suppression battery B_1; thus a complete range of backing-off voltages from +7.5 v. to −7.5 v. is possible. The three-position switch S_6 can be used to charge or discharge the integrating condensers C_1, C_2, or for direct reading and automatic recording.

The multiple switches S_1 and S_2 enable the capacitors C_1, C_2 to be charged either directly from the photomultiplier V_1—which has been found useful for calibration purposes—or from the output of V_4. These switches permit the condensers to be charged either manually or electronically and to be discharged in opposition. A switch S_{11} short-circuits the condensers C_1, C_2 thus ensuring that no charge remains in either before the next reading is taken. The input of V_4 must always be controlled by R_4 and S_5 so that the valve is operating on the linear part of its response curve, and consequently V_4 always draws a little current. A second backing-off circuit, which consists of a battery B_2, and resistors R_{11} and R_{12}, enables the recorder output to be brought to

zero, even though this current is drawn by V_4. A potential divider R_{13} and R_{14} enables the voltage produced for charging the condensers C_1, C_2 to be attenuated in order to operate a 2 mv. input recorder. When the instrument is not used with the integrating circuit, it may be used as a direct reading device, and for this purpose S_6 is switched to the through circuit position. The signal can then be automatically recorded or read directly on the galvanometer. A selection of electrolytic capacitors C_4, C_5, C_6 enables suitable damping for the galvanometer readings to be provided.

The following is a summary of a number of practical test operations of the apparatus.

The spectrophotometer was set up so as to ensure that the output of V_4 was just operating on the linear part of its response curve, when a blank solution (85% acetone, 5% HCl, and 10% water) was aspirated into the flame, and R_5 was set at 10K Ω. The recorder was then set up so that there was linearity of deflection, and so that the maximum anode current of V_4 produced a full scale reading. The essential steps of the rest of the operations were as follows: R_2 was set at 2M Ω, and 100 μl. of blank solution (held in a siliconed micro cup 27) was fed into the oxy-hydrogen flame, and S_1 switched so that the condenser C_1 would charge whilst the solution was aspirated. Next, 100 μl. of a sample solution was introduced into another siliconed micro cup 27 and S_1 arranged to charge the condenser C_2. Switches S_6 and S_2 were then operated to discharge the condensers in opposition, and the time taken for the charge to fall to some set arbitrary level on the recorder was calculated.

Operation as a direct reading instrument is very much simpler than above. R_{15} is set at zero ohms, and S_6 is switched to the through circuit position (direct reading). The setting up procedure was similar to that for integration, but in this case R_{13} was adjusted to give maximum deflection on the recorder for the most concentrated standard. Samples were introduced in either the original Beckman cups or the micro cups, and the results automatically recorded.

To operate as an absorptiometer or for normal Beckman flame spectrophotometry the signal reversing switch S_4 was set to operate the milliammeter, and the polarity of the zero suppression battery B_1 was reversed by the switch S_3.

Total atomisation of a standard volume of electrolyte solution has advantages over the partial aspiration for a definite time interval. The signal strength changes in direct proportion to the atomisation rate. The time taken for a standard volume to atomise is also directly proportional to this rate. Therefore, if the atomisation rate drops, a longer time is taken for a given volume of liquid to atomise, but at the same time the signal strength decreases proportionately. On the other hand, an increase in rate means a shorter atomisation time with an increased signal. Thus, if the total signal from a standard volume is integrated, variations in the rate of aspiration do not affect reading. Again automatic compensation is made for evaporation from aqueous solutions; here the volume decrease causes a proportional increase in the signal.

With samples dissolved in acetone, some evaporation occurred during the time of aspiration, and as much as ±5% error was found. This was reduced to ±2% by atomising immediately after removing the sample from a closed vessel. Normally evaporation would not cause such errors, but in this case, when acetone evaporates, differences are caused due to its enhancing effects. Acetone enhances the signal from most of the 45 elements detectable, and thus increases sensitivity.

The sensitivity of the methods when the instrument is used with the integrating circuit and an enhancing solvent is greater than any other hitherto described.

The instrument can also be used as a direct recording device without the integrating circuit. Quantities of 0.1–01.0 μg. of magnesium and calcium in liver mitochondrial preparations and cerebrospinal fluid can be determined with an accuracy of ±3%. Sodium concentrations in the range 1–1.2 p.p.m. were automatically recorded with an accuracy of ±2%.

Although in the foregoing particular description of one practical embodiment of the invention, a recognised commercial spectrophotometer was used, it will be understood that this was purely a matter of technical convenience, and does not constitute an essential feature of the invention.

I claim:

1. A flame spectrophotometer of the aspirator type including a burner; a vessel for containing an electrolyte solution; means for feeding said solution to said burner, a pair of electrodes located so as to dip into the solution in said vessel during feeding thereof to the burner; an electrical switching circuit including said electrodes; an output circuit including an integrating device; and a photoelectric transducer for viewing the flame of said burner to provide a current to said integrating device, said switching circuit serving to couple the output of said transducer to said output circuit and to terminate integration by said integrating device when said solution is decreased to a level below said electrodes.

2. A flame spectrophotometer of the aspirator type including a burner; a vessel for containing an electrolyte solution; means for feeding said solution to said burner, a pair of electrodes located so as to dip into the solution in said vessel during feeding thereof to the burner; an electrical switching circuit including said electrodes; a photoelectric transducer for viewing the flame of said burner; and an integrator circuit coupled to said transducer through said switching circuit which serves to terminate integration by said integrator circuit when said solution is decreased to a level below said electrodes.

3. A flame spectrophotometer of the aspirator type including a burner; a vessel for containing an electrolyte solution; means for feeding said solution to said burner, a pair of electrodes located so as to dip into the solution in said vessel during feeding thereof to the burner; an electrical switching circuit including said electrodes; a photoelectric transducer for viewing the flame of said burner, an integrating condenser coupled to the output of said photoelectric transducer through said switching circuit which serves to terminate integration by said condenser when said solution is decreased to a level below said electrodes; and an indicator constituting an output circuit for the discharge of said integrating condenser.

4. A flame spectrophotometer of the aspirator type including a burner, a vessel for containing a solution to be fed to said burner; a conductivity switch associated with said burner and adapted to complete an external circuit only during feeding of said solution to said burner; a photoelectric transducer for viewing the flame of said burner; and an integrator circuit for integrating the output of said transducer and energised through said conductivity switch which serves to terminate integration by said integrator circuit when said solution is decreased to a level below said electrodes.

5. A flame spectrophotometer of the aspirator type including a burner, a vessel for containing a solution to be fed to said burner; a conductivity switch associated with said burner; relay means operated by said conductivity switch, a photoelectric transducer for viewing the flame of said burner; and an integrator circuit connected by said relay means to the output of said transducer, said conductivity switch operating the relay means to cause integration by said integrator circuit only during aspiration of the solution by the burner.

6. A flame spectrophotometer including a burner of the aspirator type, a vessel for containing a solution to be fed to the burner, means for feeding said solution to said burner, a photoelectric transducer for viewing the flame of said burner, an integrator circuit connected to the output of said transducer, and detector means asso-

ciated with the burner for detecting the presence of solution being fed to the burner, which detector means serves to complete the integrator circuit only during feeding of said solution to the burner and to terminate integration by the integrator circuit when said solution ceases to be fed to the burner.

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