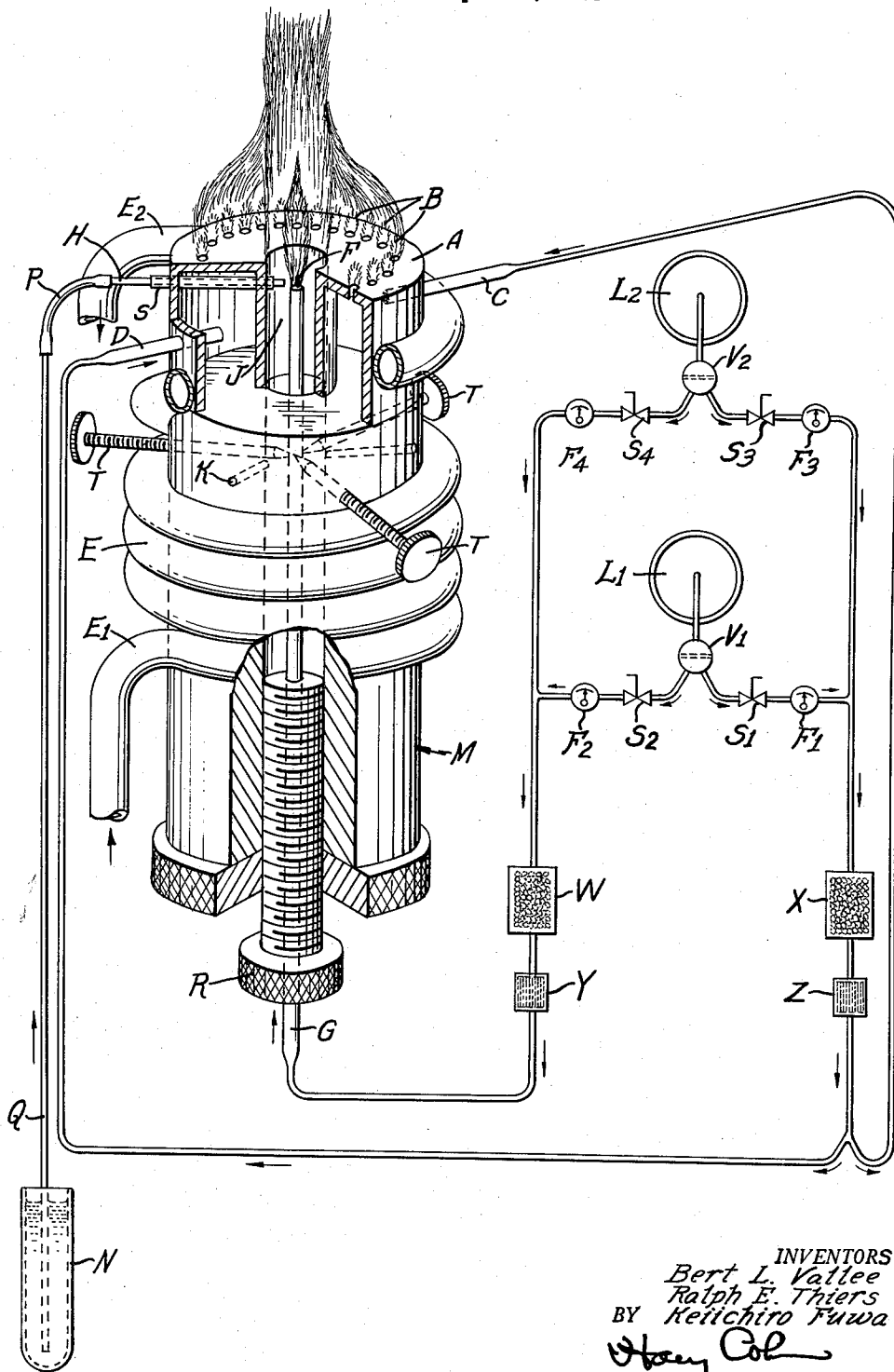


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SPECTRAL FLAME BURNERS AND SYSTEMS

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This invention relates to flame photometry and more particularly to a burner and burner system for use in chemical spectroscopy.

In the publications of Vallee and Baker, Anal. Chem. 27:320 (1955), Vallee and Baker, J. Optical Soc. America 45:773 (1955), Vallee and Bartholomay, Anal. Chem. 28:1753-55 (1956), the cyanogen-oxygen flame is described as being far more sensitive a spectrochemical flame source for analysis of trace metals than any previously described flame. Thus, concentrations varying from 0.36 to 36.0 parts per million of metals such as aluminum, barium, calcium, cobalt, copper, iron, lead, magnesium, manganese, nickel, and strontium can be determined as well as the alkali metals, which latter are quantitatively measurable by other previously described flames. The greatly improved sensitivity of the cyanogen-oxygen flame compared with other flames is attributed to its high temperature whereby adequate energies are provided to excite elements requiring high excitation energies.

Flame photometer burners presently available on the market are not suitable or operable with safety for providing a cyanogen-oxygen spectral flame. In using certain of such burners for a cyanogen-oxygen flame, we have found them objectionable, deficient, and dangerous principally because (1) a comparatively large quantity of the sample liquid is required, (2) it is difficult if not impossible to provide a flame which can be controlled to burn in an advantageous size and shape, (3) there is danger of serious explosions, and (4) there is danger of the flame becoming extinguished without interruption of the flow of poisonous cyanogen gas through the burner.

The burner and burner system, provided in accordance with our present invention, is based upon our discovery that a highly satisfactory cyanogen-oxygen flame can be provided if the cyanogen and oxygen are mixed in equimolar proportions and if the equi-molar mixture is supplied to the burner both for combustion to provide the flame and for aspirating the sample liquid for introducing it into the flame and if an equi-molar cyanogen-oxygen mixture is simultaneously supplied to form an auxiliary flame adjacent to the flame into which the sample liquid is introduced.

The pre-mixing of the cyanogen and oxygen gas in equi-molar proportions prevents explosions which would occur if these gases were supplied separately to the burner. For example, in one well known type of spectral flame burner, the combustion gas or fuel such as acetylene or hydrogen is supplied to the burner simultaneously with the introduction of a stream of oxygen to support combustion of the fuel and to aspirate the sample liquid in atomized form into the flame. If cyanogen were substituted for the fuel in this known type of burner and supplied thereto without first pre-mixing it with oxygen in equi-molar proportions, there would be an intolerable danger, if not certainty, of the occurrence of explosions.

In the burner system of the present invention, the stream of the cyanogen-oxygen mixture is employed as above stated, not only to provide the combustible mixture for the flame but also to introduce the sample liquid into the flame in contrast with the above mentioned presently marketed burners in which the combustion supporting gas, namely oxygen, in the form of a separate stream, is

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used for aspirating the sample liquid as well as for supporting combustion of the separately supplied fuel for the flame. However, the use of the cyanogen-oxygen mixture, pursuant to our invention, for aspirating the sample into the flame as well as the combustible mixture for producing the flame makes advisable the provision of an auxiliary flame adjacent the flame into which the sample liquid is introduced. This is due to the fact that, on the one hand, the flame propagation speed of a cyanogen-oxygen mixture is low in comparison with the rate of flow of the mixture required to induce, by aspiration, an optimal flow of the sample liquid into the spectral flame, while on the other hand, the rate of flow of the gaseous mixture required to aspirate the sample liquid at an optimal rate of flow, is too high in comparison with the flame propagation speed of the mixture so that in the absence of the auxiliary flame, the spectral flame would not continue to burn. It is to be noted, however, that while in our burner, hereinafter described, the gaseous mixture supplied to the burner for the auxiliary flame prevents the spectral flame from being self-extinguished, as a result of the high flow rate in comparison with the flame propagation speed of the gaseous mixture, the burner is so constructed that the sample liquid is not introduced into the gaseous mixture which is supplied for the auxiliary flame. Further, it is to be noted that the auxiliary flame is not a part of the main or spectral flame but is operable to sustain the main flame.

Briefly described, the spectral flame burner of this invention comprises a main body having means providing a spectral flame zone, means adjacent to said spectral flame zone providing an auxiliary flame zone, means for supplying to each of said zones a combustible mixture consisting essentially of a gaseous fuel and combustion-supporting gas, and a liquid-sample feed having an outlet in direct communication with said spectral flame zone and segregated from said auxiliary flame zone whereby the sample liquid is introduced only into the spectral flame and the auxiliary flame devoid of sample liquid aids in sustaining the spectral flame in said spectral flame zone.

The above and other objects, features and advantages of this invention will be fully understood from the following description of the presently preferred embodiment of our invention considered in connection with the accompanying drawings which are to be considered as illustrative of the invention but not in limitation thereof.

The drawing is a view of the burner system and shows an enlarged perspective view, partly in section, of the burner.

The details of the burner are shown in the diagrammatic sketch of FIGURE 1. Both the main burner and the auxiliary burner by which it is surrounded are supplied by pre-mixed cyanogen and oxygen gases. Gases flowing from capillary tube G form the main or spectral flame, the base of which is at F. This tube, fashioned of platinum or palladium, is 5 cm. long, O.D.—0.5 mm., I.D.—0.3 mm. It is soldered into its support, the threaded brace fitting R. Capillary G can be adjusted vertically by rotation of R and horizontally by means of the screws T.

The auxiliary flame burner consists of 24 apertures B, forming a ring of small, individual flames in the hollow ring A, of O.D.—1.5 cm. and surrounding a central, cylindrical space, 0.5 cm. in diameter. It is fastened to the body of the burner M by a joint of silver solder. Water for cooling is passed through the helical copper tubing E entering at the inlet E1 and discharging at the outlet E2. The sample enters the flame via capillary H which passes through a hole in ring A.

Details of the sample capillary and the gas capillary G are shown in the drawing. A piece of stainless steel tubing S (syringe-needle, size No. 23) is soldered into

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the hole through ring A and supports the silica capillary H, which is cemented into its lumen. Tube H consists of a capillary drawn from silica tubing so that its outside diameter is between 0.02 and 0.3 mm. Three horizontal apertures, K, 1 mm. in diameter are set at an angle of 120° in the middle section of the main body of the burner M to supply air at atmospheric pressure to the chamber J to relieve a partial vacuum which might form due to the fluid flow in the upper part of this chamber and to aid in shaping the auxiliary flame around the spectral flow adjacent thereto.

The gas supplies for the auxiliary and main flames are shown schematically in the drawing. Oxygen and cyanogen are supplied from cylinders L1 and L2, respectively, which are equipped with diaphragm valves V1 and V2 to reduce the tank pressure for each gas to 20 lbs. per square inch. From diaphragm valve V1 oxygen is led through two ¼ inch copper tubes to needle valves S1 and S2 which control its rate of flow to the pilot and main flames respectively. The flow rates are measured by flow meters, F1 and F2. Similarly, cyanogen gas is led from diaphragm valve V2 through two ¼ inch copper tubes to needle valves S3 and S4 and flow meters F3 and F4. Oxygen and cyanogen from F1 and F3 respectively are then combined to form the auxiliary flame and from F2 and F4 to form the main flame. In each case the gases are mixed in a copper tubing, indicated at W and X, which is 4 centimeters in length and filled with Pyrex glass beads and then passed through the fine capillary tubes Y and Z. The copper tubing for the main flame is led directly to the base of capillary G. The tubing to the auxiliary flame burner is split, and the mixed gases are led into ring A via antipodal tubes C and D.

The operation of the burner system, according to a preferred example, is as follows:

Needle valve S3 is opened until flow meter F3 indicates cyanogen flow of 350 ml. per minute; the pilot flame is then lit with a match. Needle valve S1 is then turned until flow meter F1 registers 350 ml. of oxygen per minute. When the pilot flame has been adjusted properly, needle valve S4 is opened to admit cyanogen gas to the main flame, and the rate is adjusted to 480 ml. per minute. Finally, needle valve S2 is adjusted until the oxygen flow to the main burner is also 480 ml. per minute.

The immersion of the lower end of tube H into a sample solution, contained in a microbeaker N, aspirates the sample into the flame as a spray of very fine droplets. If the volume of microbeaker N is calibrated, the flow rate of the sample may be established by observing the decrease in the volume of the sample over a measured interval of time. A fine flexible capillary tube P of polyethylene is fitted over the lower end of silica capillary H. This flexible capillary is 2.2 cm. long and fits over the upper end of a glass capillary Q, the inside diameter of which is small enough to limit the flow of sample solution through capillary H, and thereby fix the flow rate of the sample. Alternatively, sample may be forced through capillary H under pressure. For this purpose, a polyethylene capillary is attached to H, and its lower end is flared to fit over the end of a 0.1 milliliter drawn-tipped pipet, which contains the sample. Any chosen flow rate may be obtained by applying varying gas pressures to the other end of this pipet to force the sample through capillary H. The flow rate of the sample may be determined by measuring the time required for the meniscus of the sample solution to reach successive calibration marks of the pipet.

Adjustment of the relative positions of tubes G and H at any given rate of sample flow results in smooth aspiration and small, uniform drop size. This adjustment is accomplished by means of the 3 horizontal screws T while the flame is in operation.

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The intensities of the spectral lines exhibit sharp maxima at flow rates of the order of 0.06 milliliters per sample per minute; therefore, the flow of the sample must be capable of accurate and reproducible regulation. The sample is aspirated from the capillary H into the main flame by the very rapid stream of pre-mixed gases from the orifice of tube G. By alteration of the resistance which capillary H offers to the flow of the sample, the rate of sample aspiration can be varied reproducibly. When the sample is aspirated directly from the microbeaker, the chosen rate of flow may be obtained by variation of the dimensions of capillary H. A very wide range of flow rates may be obtained by the use of capillaries of various internal diameters and lengths. Alternatively, a set of glass capillaries Q of varying lengths and diameters can be manufactured and calibrated for insertion into the lumen of the fine polyethylene tube P which forms an extension of the fused silica capillary H. These capillaries may be employed to modify flow and provide a range of sample flow rates without requiring a change of the silica capillary. The flow rates for any given arrangement can be measured and typical values for capillaries of different interval diameters and lengths are shown in the following table:

Dimensions of sample-feed capillaries of calibrated flow rate

Internal Diameter, mm.	Length, cm.	Observed Flow Rate, ml./min.
0.2	1	0.15
0.2	2	0.10
0.2	3	0.05
0.1	1	0.013
0.1	2	0.01
0.1	3	0.005

Direct attachment of a pipet to the polyethylene capillary P, and the application of controlled pressure to the other end of the pipet can be used to provide a still wider range of sample flow rates, if required for special purposes.

The velocity of flame propagation in equi-molar mixtures of cyanogen and oxygen is quite low, and as a result a simple flame of this mixture cannot be maintained at high rates of gas flow from a small burner orifice. On the other hand, a high exit velocity is required if the pre-mixed fuel gases are to aspirate the sample solution into the flame as a fine spray. The range of linear velocities at the exit over which a stable flame can be obtained is very narrow. At the upper limit the simple cyanogen-oxygen flame blows itself out and this limit is far below the velocity required to aspirate sample solution. At the lower limit the flame backs down the tubing toward the mixing point. The pilot flame resolves this dilemma by maintaining the stability of the main flame at speeds of gas flow far in excess of those otherwise possible, thus permitting effective aspiration of the sample. The slow velocity of flame propagation proves to be an asset rather than a handicap in the system for conducting gases from the tanks to the burner. This permits the combustion of a pre-mixed equi-molar mixture of cyanogen and oxygen with perfect safety. Capillaries Y and Z in the conduction lines are made small enough so that the mixture of the gases flows through them at a speed greater than that of the flame propagation. Thus, the flame cannot "strike back" beyond these capillaries. Because of the extremely high flame temperature, the burner is preferably cooled during operation by passage of tap water through coil E.

It will be observed that the sample-feed capillary tube H and the gas supply tube G are not concentric. On the contrary, unlike the arrangement of the sample-feed and gas feed passages of currently conventional spectral flame burners, the sample-feed tube H of our burner is dis-

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posed transversely of the gas feed tube G. This tube arrangement aids to a considerable degree in the ability of the stream of gas issuing from the outlet of tube G at a comparatively low flow rate to aspirate the sample liquid through tube H at low flow rates and to effectively atomize the liquid and introduce it in the form of fine droplets into the spectral flame, thus effecting an economic use of the liquid, which is frequently mandatory when only small quantities of the liquid are available and also avoiding cooling of the spectral flame.

The invention of this application is related to the invention described in our United States patent application, Serial No. 651,517, filed April 8, 1957, assigned to the assignee of our present application.

While we have shown and described the preferred embodiment of our invention, it will be understood that various changes may be made therein without departing from the underlying idea and principles of the invention within the scope of the appended claims. It will also be understood that the burner of this invention, while especially advantageous for providing high temperature cyanogen-oxygen spectral flames, may be used for providing spectral flames from other combustible gaseous mixtures. Further it will be understood that the burner of the present invention may be employed with any suitable spectrophotometer without limitation as to the type thereof.

Having thus described our invention, what we claim and desire to secure by Letters Patent is:

1. In a spectral flame burner, a main body having means providing a spectral flame zone, means adjacent to said spectral flame zone providing an auxiliary flame zone, means for supplying to each of said zones a combustible mixture consisting essentially of a gaseous fuel and combustion-supporting gas, a liquid-sample feed means having an outlet in direct communication with said spectral flame zone and segregated from said auxiliary flame zone whereby the sample liquid is introduced only into the spectral flame and the auxiliary flame devoid of sample liquid aids in sustaining the spectral flame in said spectral flame zone, means for forming said combustible mixture before it is supplied to said zones, and separate means for controlling the rate of flow of the preformed combustible mixture to each of said zones.

2. In a spectral flame burner, a main body having means providing a spectral flame zone, means adjacent to said spectral flame zone providing an auxiliary flame zone, means for supplying to each of said zones a combustible mixture consisting essentially of a gaseous fuel and combustion-supporting gas, and a liquid-sample feed having an outlet in direct communication with said spectral flame zone and segregated from said auxiliary flame

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zone whereby the sample liquid is introduced only into the spectral flame and the auxiliary flame devoid of sample liquid aids in sustaining the spectral flame in said spectral flame zone, means for forming said combustible mixture before it is supplied to said zones, separate means for controlling the rate of flow of the preformed combustible mixture to each of said zones, and means for supplying from said forming means a preformed combustible mixture to said zones in separate streams respectively.

3. In a spectral flame burner, a main body having means providing a spectral flame zone, means adjacent to said spectral flame zone providing an auxiliary flame zone, means for supplying to each of said zones a combustible mixture consisting essentially of a gaseous fuel and combustion-supporting gas, and a liquid-sample feed having an outlet in direct communication with said spectral flame zone and segregated from said auxiliary flame zone whereby the sample liquid is introduced only into the spectral flame and the auxiliary flame devoid of sample liquid aids in sustaining the spectral flame in said spectral flame zone, and air passage means in said body for the supply of air in the region of the spectral flame between the latter and the auxiliary flame.

4. In a spectral flame burner, a main body having an inner open-end chamber, a combustible-gas supply tube having an outlet in said chamber adjacent said open end and providing a spectral flame zone directly at said end of the chamber, said main body having an outer chamber surrounding said inner chamber and provided with inlet means for a combustible gas and with outlet means for the formation of an auxiliary flame laterally adjacent to said spectral flame, and a sample-liquid supply tube extending into said inner chamber and having an outlet disposed adjacent to said combustible-gas supply tube with the outlet of the latter in aspirating relation to the outlet of said liquid supply tube whereby the flow of the combustible gas into said spectral flame zone induces a flow of sample liquid directly from the outlet of said liquid supply tube into the spectral flame and segregated from the auxiliary flame, and air passage means in said inner chamber for the supply of air in the region of the spectral flame between the latter and the auxiliary flame.

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